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Frontispiece.] [*Photo : Pirou, Paris.*

MADAME CURIE,

Professor of Chemistry, La Sorbonne, Paris.

RADIOCHEMISTRY

BY

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PREFACE

THE title of this book has been chosen deliberately; the science of radioactivity has developed to such an extent as to make it justifiable and convenient to divide it. Here it is treated from a chemical standpoint; the physical side is introduced only so far as is necessary to explain the special experimental methods.

The contents are largely based on three articles dealing with the "Transformation of Elements" which appeared in *Science Progress* in April, July and October 1908, and I wish to thank Mr Murray for his consent to their reproduction in this form, and for permission to reproduce several of the diagrams. My idea in writing these articles, which I have endeavoured to carry more completely into execution here, was to give an exact account of present knowledge of the chemical properties of the radioactive substances and their chemical effects. I have tried to make this account as lucid and simple as accuracy on the one hand and limitation of space on the other will permit.

I may be accused of devoting too much attention to the methods of work which have been devised in this laboratory to the exclusion of those in use elsewhere. I would reply that the methods used in the study of the chemical effects of radioactive substances are in large part applications of those originally devised here, and that from a description of these the reader will gain an insight into the essentials of all.

The book is intended to be of use to those who, having some knowledge of chemistry and physics, wish to know accurately the facts and theories of the subject at the

present time; it is also intended as an introduction for others who wish to master the subject in its entirety. For the sake of the latter a bibliography of all the more important recent work is given at the end of the book.

Chapters on the connection of radioactivity with geology and medicine have been added to render the treatment complete, and I desire to acknowledge my indebtedness in preparing these to Joly's *Radioactivity and Geology* and to Wickham and Degrais' *Radiumthérapie*.

I have frequently referred in the text to my indebtedness to Rutherford's *Radioactivity*, which is practically the final word in the treatment of the physical side of the question.

I have also to acknowledge the kindness of the secretaries of the Chemical Society for permission to reproduce figures 5, 6, 7, 13 and 14 from the Society's *Transactions*, of Messrs Taylor & Francis for like permission for figure 12 from the *Philosophical Magazine*, and of MM. Masson et Cie for permission for the chart, figure 15, from *Le Radium*.

My thanks are due to Madame Curie, Sir William Ramsay and Professor Rutherford for permission to reproduce their photographs in this volume; also to the respective photographers for like permission.

In conclusion I desire to express my sincere thanks to Sir William Ramsay for the interest which he has taken in the writing of this volume, and for the help and advice which he gave me during the preparation of the original articles.

University College,
London, *November* 1909.

RADIOCHEMISTRY

CHAPTER I

HISTORICAL INTRODUCTION

It may be considered that a science which has been in existence scarcely fourteen years can have as yet no history worth recording. But, although not born clad and armed as Minerva, the science usually termed *radioactivity* has advanced so rapidly, the mistakes of its investigators have been so few, and their interpretations so acute, that already it may be said in one sense to have reached finality; the main doctrine of the science, the successive degradation by their spontaneous disintegration of certain elements of high atomic weight to others of lower atomic weight, may be held to be proved, and alterations will take place only in details of less importance. While much important work still remains to be accomplished, it is doubtful whether many new facts will be discovered of so fundamental a character as those already made known.

The discovery of radioactivity, and the attendant discovery of radium, were not due to chance, but were the culminating links in a long series of experiments by different investigators of which certain pieces of work, and certain of the workers, stand out markedly.

Similarly the development of the subject is in great part the work of a few, and it is convenient to summarise here the researches which finally led to the discovery of radium and the theory of radioactive transformation.

It has been known for a considerable time that if a sealed glass vessel, containing two electrodes, and filled with a gas at about one-twohundredth of an atmosphere pressure (*i.e.* at a pressure of between three and four millimetres of mercury, since an atmosphere represents approximately 760 millimetres), in other words, if a *spectrum tube* * has its two electrodes connected with an induction coil, or some other means of obtaining high tension electricity (high voltage, but very small amperage) instead of the electric spark which is obtained in air at normal pressure, a broad glow fills the tube, emitting a definite spectrum, *i.e.* a particular emission of light, which varies with the gas contained in the tube.

When the tube is evacuated still further, the glow diminishes, and is succeeded finally by a green phosphorescence on the wall opposite the negative electrode, the *cathode*. The electrode is emitting *rays*, which travel in straight lines at right angles to the cathode itself. This can be shown by interrupting their path. If, previous to the evacuation of the tube, an irregular solid or disc is placed in it near the cathode, the general phosphorescence over the wall of the tube is broken by a dark patch corresponding in outline to the solid; this has cut off, reflected, all the straight rays which fell upon it. These rays are known as *cathode rays*. They have been studied exhaustively by **Lenard** and others; much of

* Compare also p. 97.

the work has been carried out in the Cavendish laboratory at Cambridge by Sir J. J. **Thomson** and his pupils.

It is now known that cathode rays are negatively charged particles of matter, whose mass is approximately one-thousandth that of the hydrogen atom, moving with velocity comparable with that of light, and capable of penetrating a considerable thickness of matter, (although this power of penetration is distinctly limited). In fact they are supposed identical with the *electrons*, the units or atoms of electricity, which function in all chemical changes, and which have been linked recently with the chemical theory of valency by Sir William Ramsay. Two of the fundamental properties of cathode rays are their photographic action, and the fact that air or gases through which they pass are rendered conductors of electricity, although usually amongst the best insulators known.

The discovery of *X* or *Röntgen rays* arose naturally from the study of cathode rays, although the actual observations by **Röntgen** in 1896 were in the nature of accident. He found that if a solid was placed in the path of cathode rays so that they were stopped suddenly, other rays of much greater penetrating power were produced, which could be detected by various properties, *e.g.* they lit up a screen of barium platinocyanide placed *outside* the vessel in which they were produced. Many of the most striking properties of these rays are well known. Their penetrability is great, but is proportional to the density of the substance penetrated. Hence they penetrate flesh far more readily than bone, and this property has caused their extensive use in surgery.

The theory of Röntgen rays which is most generally accepted was put forward originally by Stokes, who considered that the rays were electro-magnetic pulses, ether vibrations, produced by the sudden collision of cathode rays and whatever they impinged on. They are comparable with ordinary light but of much shorter wavelength than even ultraviolet light.*

Goldstein discovered that when the cathode of a tube producing cathode rays was perforated, other rays were projected through this from the anode, and also produced phosphorescence on the walls of the tube. From the fact that they were obtained through canals in the cathode, Goldstein named them *canal rays;* they are frequently termed *positive rays.* The elucidation of the nature of these canal rays is largely due to Wien and to Thomson. Whereas the cathode rays are charged negatively with electricity, and are strongly deflected by an electromagnet, the canal rays are charged positively and can be deflected only very slightly. The deflection is in the opposite direction. They move with considerably less velocity, and their masses are of the same order as the hydrogen and helium atoms. They have not yet been identified conclusively with either of these elements.

After the discovery in 1896 of the Röntgen rays, various physicists examined different substances which occur in nature to see whether any of these possessed the property of emitting penetrating radiations. The first important advance was made by Henri Becquerel, who found that potassium uranyl sulphate emitted rays which acted on a photographic plate enveloped in black paper, and even

* Compare p. 97.

separated from the uranium salt by thin plates of metal, and other opaque substances. He found later that all the compounds of uranium, and the metal itself, possessed the same property. They not only appeared capable of giving off these radiations continuously, thus giving rise to a continuous source of energy, but they seemed perfectly unchanged in so doing.

This *spontaneous* production of rays differentiated the action of the uranium salts from that which produces the rays previously mentioned. Since radioactive substances are defined as those which possess the property of *spontaneously* emitting such penetrating radiations or rays, *uranium* is the first element in which the property of radioactivity was discovered.

It is of some interest to remember that the word *ray* was first used in a definite sense by Newton, who employed it to indicate both undulations, and corpuscles travelling in straight lines, in the latter sense especially in defending the old corpuscular theory of light. As we have seen, the expression has the two significations in the rays from a spectrum tube, and we shall see that both kinds of radioactive rays exist.

The rays from uranium salts, besides their photographic action, also render air a conductor of electricity, and are thus capable of discharging any electrified body near which they are placed. A charged *electroscope* consisting of strips of gold or aluminium leaf suspended from an insulated support, and separated from each other by the repulsion of their electric charge, is slowly discharged in the presence of a uranium salt, or other radioactive material. It can

thus be used to test for radioactivity. Not only is the electricity discharged by radioactive materials, but the rate at which the leaves fall together varies with the *degree of radioactivity*, when other conditions are the same. Different uranium salts discharge an electroscope at different rates; they have different *activities*. Madame Curie has shown that this difference is due, primarily, to the varying proportion of uranium; the radioactivity is proportional to the percentage of uranium in the salt employed. When she extended these quantitative measurements to uranium minerals, this relationship was found to hold no longer. Certain varieties of *pitchblende*—which consists largely of uranium oxide—were four times as radioactive as the uranium they contained. *Chalcolite*, copper uranium phosphate, was twice as active; the same substance prepared in the laboratory gave a figure agreeing with theory. These differences led M. and Mme. Curie to analyse systematically the mineral pitchblende; they used the degree of activity as a test for every precipitate, and separated by repeated operations the radioactive from the inactive precipitates. In this way the two elements *polonium* and *radium* were isolated in 1898.

In the same year Schmidt and Mme. Curie found independently that *thorium*, its compounds, and the minerals containing it, possessed similar radioactive properties, whilst in 1899 Debierne discovered an entirely new radioactive element in pitchblende, which he named *actinium*.

By similar methods, during the last twelve years, no less than *twenty-six new elements* have been discovered,

most of them radioactive. The history of science shows no parallel with the advance made in this subject. It is comparable with half a century's work in other directions.

The co-ordination of the rapidly accumulating facts was facilitated enormously by the series of papers published in the *Philosophical Magazine* during 1902-1903 by **Rutherford** and **Soddy**. They postulated a gradual breaking down of one element into another, with evolution of helium in the process. In this way twenty-eight radioactive elements can be classified in three divisions; the progenitors, or parent elements, are respectively uranium, thorium, and actinium. It has been proved that radium is in the line of descent from uranium. Recent work has shown that potassium is definitely, rubidium slightly, radioactive, but the alkaline metals have not been otherwise connected with the three series of elements mentioned.

The most striking proof of Rutherford and Soddy's theory, and the first actual demonstration of element-transformation, was the discovery by **Ramsay** and Soddy in 1903 that *radium continuously produces helium*, the lightest of the inactive gases, and discovered by Ramsay himself only so recently as 1896. Much of the work recently published by Ramsay and his co-workers has led to theories which, while as yet they are far from being substantiated, are of intense interest in connection with the sub-structure of matter.

The continuous evolution of energy in the process of element degradation is chiefly in the form of heat. The vast amount of heat liberated by the total quantity of the earth's radioactive material has profoundly modified

various geological theories, especially those connected with the age of the earth, and the source of terrestrial and also solar heat.

Since the first discovery of radioactive substances their medical and biological actions have been the subjects of many researches. In consequence of the small quantities of material available, less progress has been made in this branch of the subject than in others. And although much has been discovered we may expect further developments of importance.

CHAPTER II

RADIOACTIVE METHODS ILLUSTRATED BY THE THORIUM SERIES OF ELEMENTS

A NEW element is discovered in various ways. Originally it was found that particular treatment of certain ores isolated substances which possessed characteristic properties; these were considered consequently to be elements. As the study of these properties advanced, and the means of detecting or differentiating them became more delicate, the number of elements which could be distinguished from each other increased also. Investigation of a new mineral gave a substance obeying some of the tests for known elements, but not all. Further examination of this substance showed that it possessed new characteristic reactions of its own. It was a new element. Later physical properties became utilised. The distinctive *spectrum* of the elements has led in recent years to the discovery of many of the so-called "rare earth" elements. To mention yet another source of discovery, the observation by Lord Rayleigh of a slight difference between the densities of atmospheric nitrogen and nitrogen prepared from salts containing it, led to the classic discovery of argon by Rayleigh and Ramsay.

The commoner elements were first discovered, and although there are marked exceptions, still, speaking

generally, the lateness of discovery is in order of rarity of the element, and due to the increased delicacy of the method of detection. Previous to the discovery of the radioactive elements, the spectroscope afforded the most delicate means of discrimination. But the majority of these elements exist in such minute quantities that they require a far more delicate method. Only a few have been obtained in a state of sufficient purity to give a definite spectrum. We can state with certainty that the spectroscope would never have permitted their discovery.

The examination of these elements and their differentiation depend almost entirely on their *activity*, on the *nature* of the rays they emit, and on the *rate* at which these rays are emitted. It is only after from these properties the elements have been isolated in a comparatively pure condition that then they can be studied by ordinary chemical methods. We must therefore examine at some length the physical methods which here take the place of ordinary methods of analysis.

The electrical measurements of radioactivity are made with some form of electroscope or electrometer. The electroscope devised by C. T. R. Wilson, and used largely for measuring small amounts of activity, may be taken as typical. The description is that in Rutherford's *Radioactivity*, p. 86. A brass cylindrical vessel (or very frequently a tin can) is stoppered at the metal mouthpiece M (fig. 1) by an ebonite cork or an ordinary cork covered with sulphur. Through this passes a metal rod R, supporting a sulphur bead S, which supports and at

the same time insulates a narrow brass plate B some two or three inches in length. To the upper end of the brass plate is attached a leaf of gold, or better, aluminium, A. The sliding metal rod CC' is used to charge the leaf system, usually by touching it with a charged rod of sealing-wax while it is in contact with B. R is earth-connected and C revolved to break the contact with the brass and aluminium. The charged aluminium leaf is repelled through a considerable angle. Its movement is observed by a telescope through windows in the brass or tin vessel. The telescope carries a scale; observations are made of the time taken by the falling leaf to traverse a certain fixed portion of that scale. The bottom of the vessel is usually removable, the substances to be tested for radioactivity being thus introduced. In testing gases an airtight apparatus is used and the gases are introduced through metal stopcocks.

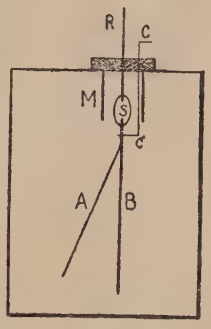


FIG. 1

Under ordinary conditions, in the absence of radioactive matter the time taken by the falling leaf to pass over the fixed portion of the scale is termed the *natural leak* of the electroscope. This natural leak is quite inconsiderable, and the time may even amount to several hours. The presence inside the case of a comparatively weak radioactive substance reduces the leak to a few minutes, or even seconds. It is desirable to give some account of the reasons underlying this behaviour.

An electroscope can be discharged readily through the

action of several different kinds of energy. Thus rays of ultraviolet light allowed to fall on the outer disc of an ordinary electroscope, or the rays given out by a lighted candle placed near it, cause the leaves to fall together rapidly. X-rays behave similarly, and through a detailed study of their behaviour Thomson and Rutherford have put forward a theory capable of explaining the whole series of phenomena; so far it has stood the test of experience. The different rays are supposed to give rise to particles termed *ions* carrying either positive or negative charges of electricity. The initial action is a collision with an atom of the gas which the ray is traversing; an *electron*, or negative particle of electricity, is set free, the atom minus this electron exhibiting a positive charge. Each, by virtue of its charge, attracts to itself a cluster of uncharged atoms. The number in the case of the electron is estimated at about thirty; the positive cluster is smaller. Both clusters behave like ordinary charged bodies, being attracted by unlike, repelled by like, charges of electricity. Consequently in the absence of any strong electric charge in their neighbourhood they ultimately collide with each other, and their charges become neutralised. But if such ions are liberated in the neighbourhood of a charged electroscope, it will attract ions with unlike charge in sufficient number to discharge itself (since the charge on the electroscope is likewise due to the presence of free electrons, if negative, or to free positive ions).

It is found that ordinary air always contains a certain very small number of ions, and the natural leak of an electroscope is due to their presence. Again, the pro-

duction of ions is strictly proportional to the number of rays—*e.g.* if two quantities of uranium oxide are taken, one twice the weight of the other, and they are spread out in thin films of the same thickness, so that the first has twice the exposed area of the second, it will emit twice as many rays as the second; they will produce twice the number of ions, having twice the effect on the leaves of an electroscope; hence it will be discharged in half the time. Similarly if equal quantities of two radioactive materials are taken, and introduced consecutively inside an electroscope, if it is found that the rate of discharge of the first is twice as fast as that of the second, then it is said to possess twice the activity of the second. The measure of the discharge-time gives a measure of the radioactivity. By comparing the effect produced by a substance from day to day, a measure of the variation in its radioactivity is obtained.

The most convenient instrument for these measurements, however, is some form of quadrant *electrometer*, preferably the modification invented by Dolezalek in 1901. This has a very light needle of silvered paper, carrying a small mirror, and suspended by a very fine quartz fibre between the four quadrants. One pair of quadrants is connected to earth, the other to an insulated metallic plate, facing a second which carries the radioactive matter to be tested. Through action similar to that in the case of an electroscope an electric stress is set up between the two pairs. The needle, previously charged to a very high potential, is repelled from one pair of electrodes towards the other; on account of its extreme lightness it moves at a uniform rate. The time

taken to pass two fixed points is observed by means of a stop-watch. As in the case of an electroscope, this time is inversely proportional, other conditions being the same, to the degree of radioactivity of the deposit under observation. The natural leak of the electrometer is deducted from all other time measurements. The electrometer is standardised from time to time against a definite amount of uranium oxide, which is known to give a constant supply of radiation. In this way any variations in the instrument are corrected.

The photographic action of the radiations has been largely used in certain branches of the subject, but does not give good quantitative results. The method employed is the exposure of the photographic plate wrapped in black paper—to cut off phosphorescent light—to the effect of the radiations. The time of exposure varies from a few minutes, with almost pure radium preparations, to days, or even weeks, with very weak radioactive preparations. With long exposures the results are especially untrustworthy on account of the difficulties experienced through the plates fogging.

In order to show how the instruments are actually employed and deductions made, a brief account will be given of the results obtained to the present time from the study of thorium compounds. The greater part is taken from Rutherford's *Radioactivity*, second edition.

Schmidt and Madame Curie independently discovered the radioactivity of thorium compounds in 1898. Four years later Rutherford and Soddy found that the thorium hydroxide precipitated by ammonia from a solution of the nitrate was less than half as active as the original

solid salt; the filtrate on evaporation gave a residue which, weight for weight, was several thousand times more active. They named this active residue thorium X (ex-thorio). It consisted largely of impurities existing in the original nitrate; the true thorium X was present only in minute quantity, and could not be separated. It became inactive at the end of a month; in the same time the thorium completely regained its activity. They concluded therefore that thorium X was actually produced from thorium. They proceeded to study the time-rates of these processes, making electrical measurements at intervals over a long time. Their results are shown in fig. 2, A (*Radioactivity*, p. 221); the curves are typical of most of those illustrating the decay and production of radioactive matter. The initial activity of thorium X was arbitrarily taken as 100; similarly that figure was taken for the final activity of the thorium compound. The activities were expressed along the ordinates, the times from the initial measurement along the abscissæ. The initial irregularities in the curves were due to the presence in the original thorium compound of further disintegration products of thorium X; these are also radioactive, and produce their own electrical effect. They were precipitated with the thorium hydroxide; in the one case we have initially the activity due to thorium plus the disintegration products of thorium X, in the other, that of thorium X alone. The initial part of the *recovery curve* is due to their activity rapidly becoming smaller as they themselves disintegrate—more rapidly than is counteracted by the gradual reproduction of thorium X. The initial part of the *decay curve* is due

to their reproduction from thorium X, when their activity gives an added effect to the activity of thorium X itself. In both cases a time is reached when in any given interval, say a minute, as much of these substances is produced as decays in that same time. These products are then

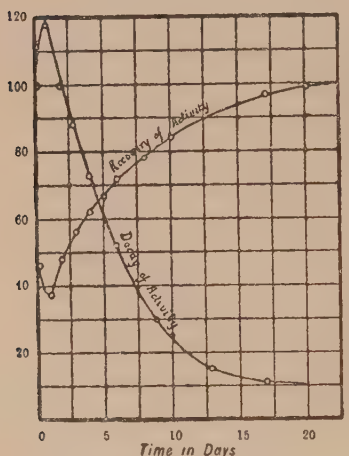


FIG. 2 A

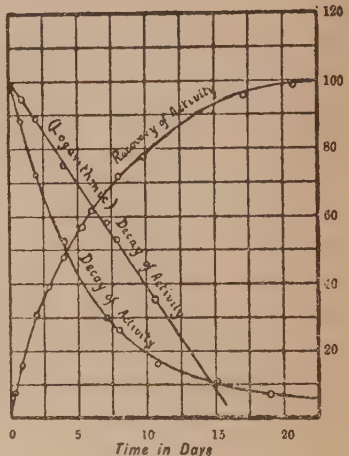


FIG. 2 B.

said to be in *radioactive equilibrium*, and no longer affect the nature of the curve. The times in question are represented by the minimum and maximum on the respective curves, and it will be noticed that these exactly correspond. If the true curves are then continued back till they meet the axis, and the maximum values in both cases again taken as 100, the corrected values are shown in fig. 2, B (*Radioactivity*, p. 222). The decay curve is *logarithmic*, that is to say, if the logarithms of the activity values are plotted against time (instead of the true

activity values), the result is always a straight line. This is shown in the figure.

Such logarithmic or *exponential* curves correspond to an equation of the type—

$$\frac{I_t}{I_0} = e^{-\lambda t} \text{ or } n.l.\ \frac{I_o}{I_t} = \lambda\ ^* \quad . \quad . \quad (1)$$

In the case under consideration I_o is the initial activity of thorium X, I_t, the activity after time t, λ is a constant and e the natural base of logarithms ($= 2.7183\ldots$).

The recovery curve is the inverse of this curve, and is represented by the equation—

$$\frac{I_t}{I_o} = 1 - e^{-\lambda t} \quad . \quad . \quad . \quad . \quad (2)$$

where I_o is the final activity (the maximum figure obtained), I_t the activity recovered after time t, and λ is the *same constant* as in the previous equation.

These results have been given in some detail because they are typical of most of the curves obtained by plotting the change of activity against time. In all cases the decay curve of the *radioactive child* bears the relation to its *radioactive parent* that the constant λ is the same for the two cases. The curves illustrate two further points. They approach constant value towards the end of a month, but it is seen that they reach a final value only at infinite time. This property is common to all such curves; it illustrates the fact that the *life* of a radioactive element is infinite. In order to compare such lives we therefore speak of the *half-life period*, a definite

* *n.l.* signifies natural logarithm.

value for each element. It represents the time in which half the element disintegrates; its activity falls to half value. This time can be calculated graphically from the curves, or from equation (1); since the activity has fallen to half value, $I_o = 2I_t$, *i.e.* $\frac{I_t}{I_o} = \frac{1}{2} = e^{-\lambda t}$. Hence if λ is known, t can be calculated. Again, λ represents the proportion of atoms changing per unit of time; $1/\lambda$ thus represents the *average life** of an atom of the element under consideration. A discussion of the meaning of these terms is given in Chapter IV. In the case of thorium X the half-time is about four days.

Hahn has recently shown that thorium at first disintegrates into **mesothorium**, and this into **radiothorium**; the last named is the immediate parent of thorium X. Radiothorium is very much more active than the thorium from which it is derived. The methods employed were similar to those just described—chemical separations, followed by measurement of the radioactivities of the different products.

Early workers on thorium noticed that the amount of radiation given off was subject to variation. Owens, in 1899, traced this inconstancy to air-currents passing over the surface of the thorium. Rutherford, next year, showed that it was due actually to a gas—hence the effect of air-currents. It could be drawn through tubes along with a current of air, passed through cotton-wool, bubbled through solutions, and gave thereafter an electrical effect. It thus behaved in every way like a true gas,

* It can easily be shown that $\frac{1}{\lambda} = t/\log 2 . \log e$, where t is the *half-life period, i.e.*, the average life is approximately 1.44 times the half-life.

although it could not be isolated, and could only be tested by its radioactive properties. Rutherford termed it an emanation. It has a very short life period. Its decay was studied by drawing it into a cylinder by an air-current, closing the cylinder, and noting the radioactivity from time to time by the electrical method (the cylinder containing insulated metallic discs connected to an electrometer). The half-life period is 54 seconds.

This emanation of course disintegrates into something else. When some quantity of it is allowed to decay in any closed vessel, the products are deposited on the walls of the vessel. They themselves give off radiations; the phenomenon is known as *excited* or *induced activity*, the deposit as the *active deposit*. It differs in chemical and physical properties from all its predecessors. The emanation can be washed out with air, and the decay rate of the deposit studied. The curve is complex; mathematical analysis indicates at least two products. These were postulated as thorium A and B. They were differentiated more clearly by the work of Miss Slater, who studied the effect of temperature on them. A platinum wire, electrically charged, was exposed for a considerable time to the action of the emanation, whereby (relatively) a considerable amount of the after-products was deposited on it. It was then heated by an electric current. A lead cylinder surrounding it caught any volatilised matter. Both wire and cylinder were then tested separately by an electrometer, the decay of the radioactivity being studied. Heated to about 700° C. the amount of radioactivity on the wire remained con-

stant, but the decay rate was faster than usual. The cylinder was at first only very slightly active, but the activity grew rapidly, the maximum being reached in four hours; the decay rate thereafter was normal. These phenomena were easily explained by the hypothesis that thorium A, the first product, volatilised below 700° and was *inactive—i.e.* gave no radiations; the thorium B, already produced from it, remained on the wire unvolatilised at 700°, and a fresh amount was slowly produced on the lead cylinder. Further work has slightly modified this result, thorium A being found to have a very slight radiation, and there being two later products, thorium B and C, all three having an extremely short-life period. The final product is inactive. So far as present knowledge indicates, the whole series is:—

Thorium → mesothorium → radiothorium → thorium X → thorium emanation → thorium A → thorium B → thorium C → inactive product.

Most of the above work has been accomplished by what may be described as the *direct method.* In addition indirect reasoning based on chemical data is frequently employed. It will be discussed more particularly in the subsequent parts of this paper. An example will be mentioned here.

The final product of the uranium-radium disintegrations is supposed to be lead, another product being helium. Boltwood has analysed a great number of uranium minerals; they all contain lead. He finds that the ratio, amount of uranium to amount of lead, varies with the age of the mineral, the older rocks giving a higher percentage of lead. This agrees with the theory

that lead is slowly produced from the uranium and radium. Strutt has analysed thorium minerals for helium; he finds evidence of some definite relationship between the quantities of thorium and helium which they contain.

CHAPTER III

THE RADIATIONS FROM RADIOACTIVE ELEMENTS

In Chapter I an account has been given of the three kinds of rays produced in a highly exhausted vacuum tube; they are, the *positive* or *canal* rays, projected with great velocity in a direction opposite to that of the electric current, and possessing mass equal to or greater than that of the hydrogen atom, *cathode rays*, or *negative particles of electricity*, actually conveying the current from cathode to anode, and *Röntgen rays*, undulations in the ether, comparable therefore with waves of light, and projected in all directions by the impinging of negative rays on matter.

Radioactive matter emits three kinds of radiation also, which are strictly comparable with these. They have been termed α, β, and γ rays or radiations. The α-rays are heavy particles, carrying a positive charge, and resemble the *canal* rays; the β-rays are electrons, as are cathode rays, and the γ-rays strongly resemble Röntgen rays.

They are frequently emitted simultaneously from active preparations.

Two properties allow of their study and differentiation: (1) they behave differently under the action of a

magnetic field ; (2) different kinds of rays penetrate matter to very different degrees.

Under ordinary circumstances all these rays travel in straight lines, as do light rays. Under the action of a very strong magnetic field the path of the α-rays becomes slightly curved; β-rays are much more easily deflected, and moreover in the *opposite* direction to α-rays—compare the fact that their electric charges are of different signs; γ-rays are not deflected by a magnetic field.

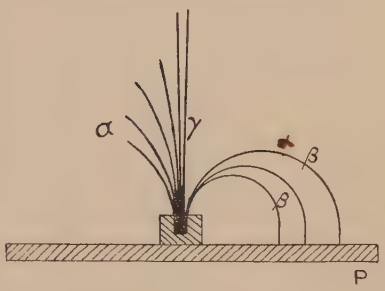


Fig. 3.

Mme. Curie has devised a simple method to illustrate these differences. Radium *in equilibrium** with its decomposition products emits all three kinds of rays. They are all cut off by certain thicknesses of lead. If a narrow cylindrical vessel of lead (see fig. 3), of sufficient thickness that no rays can pass through the walls, has a small quantity of radium placed at the bottom of it, under normal conditions, only rays projected parallel with the sides will escape from the vessel. If then, it is placed on a photographic plate P, none of the rays will affect the plate.

Under the action of a strong magnetic field, the rays no longer travel together in straight lines, but are altered as shown in the figure. The α-rays are very slightly deflected, (the curvature is purposely exaggerated in the

* Compare p. 16.

figure); the β-rays are caused to take a circular path, so that they produce a diffuse impression on one part of the photographic plate. The γ-rays alone remain unaltered.

The difference in penetrating power is shown in the following table, (Rutherford, *Radioactivity*, p. 111):—

Radiation.	Thickness of Aluminium which cuts off half the radiation.	Relative power of penetration.
α rays	0.0005 cms.	1
β ,,	0.05 ,,	100
γ ,,	8 ,,	10000

These ratios are only approximate; rays from different elements have greatly varying penetrative power. This variation further helps to differentiate the elements, and indeed itself has led to the detection of several new ones. Again, the rays are absorbed by different substances in widely differing proportions; the density of the absorbing material is one of the chief factors in determining the amount of absorption. Thus lead, a very heavy metal, absorbs most strongly, while light gases, as hydrogen, have very little absorptive power.

The radiations—as has been pointed out in Chapter II—produce ions in the gas they traverse; the mechanism is collision. Their ionising power varies very greatly, and is, in fact, roughly, the inverse of their penetrability.

The enormously greater ionising power of the α-rays supports the theory that they are heavy particles shot

off from the disintegrating atoms at enormous velocities. Such large particles cannot travel far without colliding with gas particles, hence their small penetrative power. Their great momentum produces the correspondingly great ionising effect actually observed. Rutherford has measured the velocity of α particles from different active elements; it varies from 1.56×10^9 cms. per second in the case of radium to 2.25×10^9 cms. per second for thorium C. Light travels at about 30×10^9 cms. per second. The experiments lead to the conclusion that the substances possessing longest life, *e.g.* uranium and radium, emit particles having the least velocity; the shorter the life the greater the velocity of the emitted α-ray. Rutherford has been able to measure the mass of the particle which carries unit charge of electricity; it is about twice that of hydrogen. From this he concluded, at first, that the α particle consists either of a half atom of helium (atomic weight 4), carrying one electric charge, or a whole atom carrying a double charge. More recently he has been able to identify them absolutely with particles of helium, carrying a double charge. His experiments, proving this important fact, are described in Chapter IX.

The β-rays have a greater range of velocity. The maximum velocity approximates to that of light (200,000 miles per second). Their resemblance to cathode rays has been established on three grounds: (*a*) the negative electric charge carried by both; (*b*) the ratio of that charge to the mass—extremely small in both cases—which carries it; and (*c*) the fact that a magnetic field has precisely the same effect in both cases.

α and β rays are completely absorbed by covering the radioactive matter producing them with a layer of lead 1 cm. in thickness. But even if a layer of 1 inch is used, rays still pass through. They carry no charge of electricity and are not deflected by a magnetic field, yet they ionise gases, and so affect an electrometer. These are the γ-rays, ether waves, corresponding to X-rays, but of even greater penetrating power.

All three kinds of rays on impinging on solid particles give rise to *secondary rays*, as do ordinary X-rays. The secondary rays, occasionally called δ-rays, also travel in straight lines, and otherwise obey the light laws, but are deflected by a magnetic field. They resemble cathode rays in being electrons, but move with comparatively small velocity. Ultraviolet light allowed to fall on the surface of metals produces a similar phenomenon.

In examining a radioactive substance to find what kind of radiations it gives rise to, the method in use is to cover it with varying thicknesses of aluminium. Absorption takes place to different extents; the ionisation varies accordingly; this is recorded by electric measurements. From a study of results thus obtained it can usually be determined whether one or more kinds of ray are present; the results are confirmed by noting the action of a magnetic field on rays which have penetrated the different thicknesses of metal.

The radiations produce a considerable number of effects—physical, chemical, and physiological. One of the most striking is the phosphorescence induced in many substances subjected to bombardment by the rays. Zinc sulphide, a particularly good example, is rendered

luminous by both α and β rays. Crystals of the different platinocyanides give different colour effects according to their composition. The lithium salt phosphoresces pink, the calcium and barium salts deep green, the sodium salt yellow. Willemite, a zinc silicate, becomes beautifully green in colour and apparently translucent. Kunzite shows a red phosphorescence under the action of β and γ rays; α rays are without effect on it. All strongly radioactive compounds phosphoresce strongly themselves.

The diamond not only phosphoresces when bombarded by radium rays, it also changes colour. Sir William Crookes found that a yellow diamond, after seventy-eight days' exposure to the rays, became bluish green. Prof. Bordas has recently experimented with uncoloured rubies; after some weeks' exposure they became dark brown, and in some cases pink; sapphires similarly change colour. When such artificially coloured stones are heated to 200° or 300° C, the colour is destroyed. This, however, in many cases, takes place also with the natural stones, so that the radiations permit the formation of an artificial stone of greatly enhanced value, quite indistinguishable from those found in nature. The effect in all these cases is analogous to the action on different glasses. Soda glass is coloured deep violet, potash glass a dark brown, gold glass ruby colour. Similar effects are produced by cathode rays in vacuum tubes, and by long continued action of sunlight, *i.e.* of ultraviolet light. The colour is discharged quite easily by heating the glass to 300-400° C. Maxwell Garnett has made a detailed study of these phenomena, and his

work supports the hypothesis that metallic ions are actually liberated in the glass, and that the colour is due to these, violet for sodium, brown for potassium, and so on; application of heat causes recombination with accompanying loss of colour. Other observers have endeavoured to connect these colourations, or rather the violet colouration of glass, with the presence of manganese, This explanation is much less probable. It should also be mentioned that glass tubes containing radium emanation show a beautiful green phosphorescence.

The rays produce a great number of interesting chemical and physiological effects, and it may be remarked in passing that the future of radioactivity will largely be concerned with the further study of these. The present knowledge of these effects is treated at length in Chapters VIII, X, and XIV.

CHAPTER IV

LIFE OF A RADIOACTIVE ELEMENT

A TYPICAL radioactive element gives rise continually to a radioactive product, and at the same time one or more kinds of ray are produced; radium gives rise simultaneously to radium emanation, and α rays. In addition heat in comparatively large amount is liberated continually.

This continuous production of both energy and matter has been explained by Rutherford and Soddy by the assumption that atoms of the parent element are continually breaking down, or disintegrating, into simpler atoms; the heat and rays are the difference in energy and mass contents in the two atomic systems. When gun-cotton is exploded, a complex molecule is broken up into simpler ones, while heat and light are also emitted. The two cases are parallel; the one is atomic, the other molecular.

It is found that the emanations, and many other active products, lose their activity almost completely in a measurable time. From studies of the rate at which the activity is lost, the conclusion is reached that in any one time a certain fixed proportion of the total number of atoms present spontaneously disintegrates. An actual illustration will make this clearer. The activity of any fixed quantity of radium emanation falls to half

the initial value in approximately four days. In the second four days it falls to half of this second value, *i.e.* one quarter of the original. We therefore suppose that the emanation has decomposed to a corresponding extent. In the unit of time chosen, four days, the same quantity, one-half the amount at the beginning of that period, always disappears. Similarly, in any other definite period of time, a certain quantity, bearing a definite ratio to the original amount, will disappear. Again, at the end of eight days one quarter of the whole amount remains; at the end of twelve days, one-eighth; of sixteen days, one-sixteenth. But at the end of infinite time there will always remain some quantity, however small. Similarly, in all cases of active matter some remains undisintegrated after infinite time; the radioactive elements have an *infinite life*. Though they may have *died* for all practical purposes at the end of some measurable time, an unmeasurable but definite amount remains. However, it has been shown in Chapter II (p. 18) that we can always find when half a given quantity of active substance has disappeared. And it is this period which is termed the *half-life period* of such substances. It varies from four seconds in the case of actinium emanation to millions of years in the case of uranium.

Another term constantly used is the *average life* of a substance. In Chapter II the method of calculating it has been given (p. 18). It can be conveniently illustrated by a human parallel. A church filled with people on any fixed date contains a fair assortment of men, women, and children of all ages. If we know the total number of years each person will live after leaving that church we

can calculate the *average life* of the congregation counting from the definite time fixed by that church attendance. This is quite different from the *average life* of some number of persons from the time of birth of each, which is the basis of the data employed to calculate insurance rates.

The *average life* of a radioactive element at any definite time corresponds to the first of these illustrations. If we take a definite quantity of radium salt, then the atoms of radium it contains are of all ages. If they have just previously been separated from their uranium ore some may have been *born* only a few weeks previously, others have existed thousands of years, just as the church congregation may include infants and old men of ninety. Of the radium atoms a certain number will *expire* in a definite time, just as in so many years a number of the worshippers will have died. And we can calculate the average life of the congregation of atoms with as much certainty as that of people.

The application of the second kind of *average life* to radioactive substances has been worked out in some detail by Ramsay as a lecture illustration. Though it has just been stated that the life of a radioactive atom is infinite, yet infinity is only a relative term; in this connection it only means a longer time than we can measure. It is extremely probable that just as the human life is measurable and definite, so is, let us say, the life of an atom of radium. One may go further. For there is much more regularity in the life of this dead matter; the life of human beings is variable, dependent on "all the ills that flesh is heir to," microbes, the bearers of

disease, and accidents, the ills of fortune. We have no ground to suppose that the life of a radioactive atom varies from any similar cause. For example, the rate of decay—the death-rate—of radium emanation is unaltered within the limits of measurement between the temperatures of $-180°$ and $+1600°$ C. (90 – 1870° in the absolute scale), the extremes at which, so far, it has been experimentally tested. If this tremendous difference of temperature does not hasten the decay of a single atom of emanation we can at least postulate that its life is not easily influenced by external causes. So far experimental work has shown that we cannot hasten or retard the death of a radioactive atom; consequently we cannot alter its life. For its birth is but the death of its parent atom, to which the preceding statement likewise applies. And we are justified in stating that the average life of a radioactive atom, as used in the second sense above, is in all probability the actual life of that atom.

Logically, this result applied to the preceding notion of average life, would lead to the conclusion that the average is always changing very slowly, and in fact decreasing. For if a quantity of pure radium is considered, separated from its parent element, all the atoms in it are continually ageing, and consequently their average life which remains is growing correspondingly less. The experimental evidence scarcely supports this view.

On the other hand, recent observations by Debierne, and by Rutherford and Tuomikoski, on the rate of decay of radium emanation have tended to show that it is not

homogeneous, but that the particles possess different lives, and that particles of different life possess slightly different properties. Insufficient work has yet been accomplished to enable any definite conclusions to be drawn, and the variations in life, if they do exist, are not great enough to invalidate the theory of the degradation, and the experimental and mathematical conclusions based on it. Should, however, it be proved that the emanation in a pure condition has a different rate of decay to the *diluted* gas, perhaps through interbombardment taking place in the former case, it would follow logically that a similar difference should be observable between pure radium, and radium diluted to one part in ten millions, as it occurs in nature in pitchblende.

It is also possible to imagine that the life of an atom is absolutely unalterable by external causes, but is determined by some unknown internal cause, so that the life of any particular atom may be quite an unknown quantity, whereas the average life of all is a constant determinable by the law of probability. It might then appear natural that the particular internal construction determining a particular age should be accompanied by particular properties susceptible of slight variations.

CHAPTER V

CLASSIFICATION OF THE RADIOACTIVE ELEMENTS—THEIR PHYSICAL AND CHEMICAL PROPERTIES

No fewer than twenty-six new elements have been discovered by radioactive methods; uranium and thorium were known long before their activity was observed. Of these twenty-eight elements, five are said to be *rayless;* in them no activity has been detected by the instruments in use at present. The others emit one or more kinds of ray; nine or ten give α particles alone. An appreciable life-period is possessed by nine only—uranium, ionium, radium, radio-lead, polonium, mesothorium, thorium, and radio-thorium, and actinium. The remainder are none the less true elements, although their short life may never permit them to be examined by other than radioactive means.

These twenty-six elements fall naturally into three large groups, namely, the elements uranium, thorium, and actinium, and their respective disintegration products. Using Rutherford's method of classification (from *Radioactivity*, pp. 449-50) in a slightly modified form, the elements can be grouped as shown below, Only the atomic weights of three—uranium, radium, and thorium—are known with any certainty. The α

particle is a helium atom (of atomic weight 4), and the atomic weights of the other elements, calculated by deducting 4 for each α particle evolved, may approximate to those given in brackets. The present state of our knowledge does not allow great stress to be placed on this hypothesis. In the table on the next page Ur = uranium, Th = thorium, Ra = radium, Act = actinium.

The nomenclature of the elements is due to Rutherford; his original idea was to name the first derivatives so as to show their parentage; hence Ur X, Th X, Act X (ex-uranio, ex-thorio, ex-actinio). The discovery of radiothorium and radioactinium upset this system. It will be observed that each group contains one gas or emanation; the elements derived from it are named in order of formation A, B, C, and so on. The graphic representation in the last column, due to Rutherford, illustrates the method of disintegration, the atomic contractions due to loss of α particles being considerably exaggerated in order to emphasise the theory. The brackets show those elements which differ in mass content by not more than one electron.

The figures have been corrected from the table of radioactive constants given in *Le Radium*, Jan. 1909. The life of radium given is that calculated by Rutherford from his most recent experiments.

Element.	Atomic Weight.	Half-Life Period.	Nature of Emitted Rays	Range of α-Rays in Cms. Air.	Cms of Aluminium which Absorb Half the β-Rays.	Exaggerated Graphic Representation.
First Group:						
Ur	238·5	$6 \cdot 10^9$ years	α	3·50		
↓						
?	(234·5)	?	α	?		
↓						
Ur X	(230·5)	22 days	βγ		0·048 0·014	
↓						
Ionium	(230·5)	1500 years	α	2·8		
↓						
Ra	226·5	1760 ,,	α	3·50		
↓						
Emanation	(222·5)	3·86 days	α	4·35		
↓						
Ra A	(218·5)	3 minutes	α	4·82		
↓						
Ra B	(214·5)	26·7 ,,	β		0·0078 0·053	
↓						
Ra C	(214·5)	19·5 ,,	αβγ	7·08	0·0131 0·0534	
↓						
Ra D	(210·5)	17·3 years	rayless			
↓						
Ra E_1	(210·5)	6·2 days	,,			
↓						
Ra E_2	(210·5)	4·8 ,,	βγ		0·016	
↓						
Ra F	(210·5)	143 ,,	α	3·86		
↓						
Inactive Product	(206·5)	—	rayless			

Cp. Pb=207

Th	232·5	$7 \cdot 10^{9}$ years	α	3·5
↓				
Mesothorium 1	(228·5)	5·5 ,,	rayless	
↓				
Mesothorium 2	(228·5)	6·2 hours	$\beta\gamma$	0·018 0·034
↓				
Radiothorium	(228·5)	737 days	α	3·9
↓				
Th X	(224·5)	3·71 ,,	α	5·7
↓				
Emanation	(220·5)	54 seconds	α	5·5
↓				
Th A	(216·5)	10·6 hours	slow β	0·05
↓				
Th B	(216·5)	55 minutes	α	5·0
↓				
Th C	(212·5)	? seconds	$\alpha\beta\gamma$	8·6
↓				0·044
Inactive Product	(208·5)	—	rayless	
	Cp. Bi (208·5)			

Third Group:

Act	?	—	rayless	
↓				
Radioactinium		19·5 days	α	4·8
↓				
Act X		10·2 ,,	α	6·55
↓				
Emanation		3·9 seconds	α	5·8
↓				
Act A		36 minutes	β	
↓				
Act B		2·15 ,,	α	5·50
↓				
Act C		7·36 ,,	$\beta\gamma$	0·021
↓				
Inactive Product		—	rayless	

The figures given in column five represent the maximum length of air which is traversed by an α particle before it ceases to ionise the air. It will be noticed that this length varies between the wide limits of from 2·8 centimetres for ionium to 8·6 centimetres for thorium C. In the sixth column are given corresponding data for β-rays in terms of the thickness of aluminium necessary to cut off half the rays. Here again a wide variation in the figures is seen, and this not only with different elements, but in many cases with the same element. The figures in such cases are the extremes observed, and are due to the fact that the *β radiations are not homogeneous*, but consist of bundles of rays of different velocities.

The fact that the elements potassium and rubidium show evidence of radioactivity has been mentioned. They emit β-rays, but so far no evidence has been put forward that they suffer degradation in doing so; they have in no way been connected with the above three series.

The Uranium Series.

Uranium was discovered by Klaproth in the mineral pitchblende in 1789. It is of comparatively rare occurrence, and widely scattered. The composition of uranium minerals varies largely; many are complex silicates, phosphates, or arsenates. Pitchblende and uraninite consist largely of uranium oxide, and contain from 50-80 per cent. uranium. The metal was isolated by Peligot in 1842 by the action of potassium on the fused oxide. Thus formed it is a black powder. In the

ordinary metallic state it closely resembles iron and nickel. It is volatile in the electric ore and heated to redness it burns brilliantly. It dissolves in dilute acids, with evolution of hydrogen; combines directly with chlorine, and, on heating, with sulphur. Its atomic weight is 238·5; it is thus the heaviest metal yet isolated. A great number of its compounds have been prepared. The salts are coloured, and some of them phosphoresce spontaneously. Strutt has observed a similar phenomenon with at least one of the uranium minerals. The discovery of radioactivity by Becquerel, in 1896, was made with these compounds; it has been shown that the metal is also radioactive. The life of uranium is extremely great. Its half-period is many millions of years. It belongs to the iron group of metals and is precipitated by ammonium carbonate.

In 1900 Sir William Crookes showed that when excess of ammonium carbonate is added to a uranium solution, until the uranium precipitate has all redissolved, a light cloudy precipitate remains: this contains all the photographic activity; the separated uranium is without effect on a photographic plate (α-rays scarcely affect a photographic plate; uranium gives off α-rays only); Crookes called the new product **uranium X.** The precipitate consists largely of impurities from the uranium salt, and insufficient uranium X has been obtained to give a distinctive spectrum. A mixture of ether and water effects a partial separation. The ether layer contains most of the photographic or β-ray activity. Becquerel effected a separation by adding barium chloride and precipitating the barium as sulphate;

uranium X is carried down along with it. Later (in 1906) Moore and Schlundt have described further methods of separation. When crystallised uranium nitrate is dissolved in acetone, or several similar organic solvents, the slight precipitate which remains contains most of the uranium X. Complete separation is effected by adding moist ferric hydroxide to such a solution; the hydroxide carries down all the active matter. Moore and Schlundt state that uranium X gives both α and β rays; 34 per cent. of the activity is due to the α-rays. Levin in 1907 obtained the figure 8 per cent.; in a later paper he states that no α-rays are produced, the mistake arising from the presence of β-rays of small velocity. He has since confirmed this result. Uranium X is volatile in the electric arc but less so than uranium. Uranium X has a half-life period of twenty-two days. In less than a year it has disintegrated almost completely. Into what has it changed?

Ever since Madame Curie succeeded in obtaining radium from uranium minerals, and the theory of disintegration was put forward, it has been considered highly probable that radium is a *descendant*, in perhaps the third or fourth generation, of uranium itself. Some experiments of Soddy in 1904 gave the first proof of this statement. He took about two pounds of uranium nitrate, dissolved it in water, and repeatedly added barium solution, precipitating the barium as sulphate. In this way the solution was practically freed from radium, which is precipitated along with the barium sulphate. In 567 days the solution contained more than one hundred times as much radium as it did immedi-

ately after this treatment. This radium was identified by the decay rate of its emanation. The actual amount of radium observed was only one-thousandth of what it should be on the assumption that uranium X was the parent of radium. Soddy postulated one or two intermediate products. Boltwood criticised his method of procedure but afterwards confirmed his results. In 1906 he suggested that the intermediate product was actinium. Soddy and Mackenzie, and also Rutherford, showed that this was impossible, pure uranium nitrate neither giving rise to actinium nor its emanation. Rutherford separated the actinium from solutions of commercial uranium nitrate, and by passing ammonia and sulphuretted hydrogen gases through the actinium solution, he effected the separation of a new radioactive substance, which he considered to be the actual intermediate product between uranium X and radium. Boltwood confirmed this result. He stated that this new element emits α rays (actinium is rayless) which are very easily absorbed, and β rays of small penetrability. The activity is of the same order as that of radium. He suggested the name **Ionium**. Hahn has confirmed his conclusion by a different method.

Radium was discovered by Madame Curie in 1898. Her method of procedure has been indicated. Thoroughly examining the different group precipitates in an analysis of pitchblende, she found that the barium group precipitate was strongly active. The active constituent could be separated completely along with barium sulphate. Final separation was brought about by recrystallising the barium as chloride; radium chloride is slightly less

soluble, and separated to a greater extent in the first fraction. By repeated fractionations of this nature crystals were obtained eventually which were nearly two million times as active as uranium. The activity was too great for comparative measurements; the final fractions were tested for purity by estimating the residuum of barium spectroscopically.

Giesel showed later that the separation could be effected more expeditiously by recrystallising the bromides; the difference in their solubilities is greater than in those of the chlorides.

The most recently published method for the separation of radium *ab initio* from its ore, is that published by Haitinger and Ulrich in 1908. They were furnished with 10,000 kilograms of residues from 30,000 kilograms of pitchblende, which contained 53·4 per cent. of uranium oxide, U_3O_8. From this, in the course of two years, they separated for the Austrian Government nearly three grams of radium in a state approaching purity. The radium was initially present as sulphate, and radium sulphate is more insoluble than barium sulphate.

The greater part of the soluble sulphates was removed by washing with water; the residue was digested on the waterbath with excess of fairly strong hydrochloric acid, and then again washed with water. The portion soluble in the acid contained no radium, but all the polonium and actinium. The residue was heated with half its weight of 25 per cent. sodium carbonate (free from sulphate); the mass was washed till soluble sulphates were removed, then hydrochloric acid was added. This

treatment was repeated three times. The radium was all contained in the acid extract; this was treated with sulphuric acid, which precipitated the sulphates of lead, the alkaline earths, and the rare earths. These were heated repeatedly with an excess of concentrated sodium carbonate, and the mass was then warmed with hydrochloric acid, and lastly, with water. The latter removed lead chloride, which was purified by recrystallisation and used for the preparation of radio-lead. This process was repeated several times.

The acid extract containing the radium was freed from lead with sulphuretted hydrogen, evaporated to dryness, and the greater part of the calcium chloride extracted from the residue by concentrated hydrochloric acid. The crude residue weighed, when moist, 20 kilograms, and consisted of the chlorides of radium, barium, strontium and calcium, besides small amounts of other metals. The radium chloride was the least soluble constituent. By repeated fractional crystallisation the original 20 kilograms was separated into two parts, one, 2 kilograms, containing nearly all the radium, the other, 11 kilograms, containing scarcely any. The two kilograms were fractionated until the head crop of crystals weighed only 9 grams. This was dissolved in water, freed from impurities by sulphuretted hydrogen, and re-fractionated in silica vessels. After many more fractionations, five portions were obtained. The least soluble gave an atomic weight for the metal of 225, and weighed about half a gram. It was found that, calculated as anhydrous radium chloride, $RaCl_2$, 3·236 grams were obtained in different states of purity; this corresponded to 30,000

kilograms of pitchblende, *i.e.*, the amount of radium in the latter (as metal) is less than one part in ten millions.

The fact that radium compounds have been isolated in a state of comparative purity, and in amounts much larger than those of the other active elements, has led to a more complete study of this element. The amount of radium salts actually prepared in any state approaching purity is probably still less than twenty grams, though it is now rapidly increasing. It is in existence chiefly as bromide and chloride. Nearly two hundred tons of pitchblende—chiefly from the mines at Joachimsthal in Bohemia—were worked up in order to obtain this extremely small quantity. Only three or four investigators have quantities of half a gram or more; most of the radioactive experiments have been carried out with quantities of from two or three to fifty or sixty milligrams. It is impossible to obtain any appreciable quantity, not only on account of its price—at present perhaps £5 a milligram—but especially because of the limited amount which has as yet been prepared. The output of the Joachimsthal mine is controlled by the Vienna Academy of Science, to whom much credit is due for its loans of large quantities of radium preparations to several of the most distinguished workers in this line of research, whereby much important work has been accomplished. Recently, however, the Austrian Government has forbidden the export of radium from the country. It is probable that the new Radium Company in connection with the Trenwith Mine in Cornwall will be the source of most of the radium used in this country in the future.

The chloride, bromide, sulphate, and carbonate of radium are known. The metal has not yet been isolated; this is due both to the necessary minuteness of the operations and the great risk of loss. The salts strongly resemble those of the alkaline earths, especially barium, and are given corresponding formulæ. The sulphate, $RaSO_4$, is even more insoluble than barium sulphate; the crystallised bromide, assumed to be $RaBr_2$, $2H_2O$, is somewhat less soluble than $BaBr_2$, $2H_2O$. The salts colour a flame crimson, as do strontium salts. The spectrum was first examined by Demarçay, and has been studied more recently by a number of other physicists. In its general aspect it resembles the spectra of the other alkaline earth metals.

The salts are quite white when freshly prepared; they are all spontaneously luminous; in other respects, they closely resemble barium and calcium salts. On long standing they turn first yellow, and finally brown. It is found that the colour is much deeper with impure preparations; pure salts are scarcely coloured after a considerable period. This can be used as a test of the degree of purity.

All the radium salts are radioactive; it is practically certain that the metal would exhibit the same radioactive properties, and disintegrate in the same way. There are several grounds for this statement. Uranium has the same radioactive properties, whether free in the state of metal or combined in its salts. When a solution of radium bromide is electrolysed, the mercury becomes permanently active, showing the formation of radium amalgam. This shows the same radioactive properties of its salts. Several

radioactive elements have been deposited on metals, that is, they have been deposited in metallic form themselves. One example is polonium or radium F, separated by placing a rod of bismuth in a solution of its salt; it possesses the same activity as metal as it does in solution.

Direct determinations of the atomic weight of radium have been made by Madame Curie. In her initial experiments, by successive crystallisations of barium chloride she obtained fractions increasing in atomic weight from 137·5 (barium) to 225. The final fraction weighed only 0·1 gram. Much later, in 1907, she worked up 0·4 gram of chloride of such purity that its spark-spectrum showed that only minute traces of barium were present. By precipitating the chloride as silver chloride with warm silver nitrate solution the ratio Ra: Ag was obtained. Three successive determinations of the atomic weight with the same fraction gave as mean value 226·18. Madame Curie concluded that the atomic weight is 226·2±0·5.

More recently Thorpe has published the results of his determinations, using Madame Curie's methods. The spectrum of his final preparation of radium chloride scarcely showed the presence of the strongest barium lines. Three successive determinations of the chloride as silver chloride made the atomic weight of radium respectively 226·8, and 225·7 (mean 226·7). Until further work has been completed the figure 226·5 may be accepted as approximately correct.

From certain series of lines in the spectrum, analogous with those of calcium, strontium, and barium, indirect determinations of the atomic weight have been made by Runge and Precht, and by Marshall Watts; the former

deduce an atomic weight of 258, the latter a weight agreeing with Madame Curie's figure. Watts has pointed out an error in Runge and Precht's arguments, and has given an interpolation formula for the barium radium series of elements.

The time of decay, and the life of radium have been fixed from several lines of evidence. It will be dealt with later.* The product of the decay is that gas or emanation discovered by Dorn in 1900.† It can be pumped off from radium preparations or carried away by a current of air; obtained in this way its rate of decay has been examined by a number of investigators. Rutherford and Soddy's first determination was 3·71 days (half-life); the Curies obtained the figure 3·99 days, Sackur 3·86. Recently (in 1907) Rumelin, working under Rutherford, obtained the value 3·75 days (the mean of eight experiments; the limits were 3·70–3·80).

On account of the ease with which small quantities of gas can be separated, tested, and purified in comparison with small quantities of a solid, and of the fact that this is the only emanation which has an appreciable life (the half-life period of thorium emanation is 54 seconds, of actinium emanation 4 seconds), it has been examined more completely than any other radioactive substance.

Rutherford and Soddy, and later, Ramsay and Soddy, demonstrated beyond all doubt its peculiar inertness by

* See p. 68 *et seq.*

† According to Hahn and Meitner, radium emits β rays of small penetrability. They attribute these, not to radium itself, but to a hypothetical element, radium X, which they have not yet succeeded in isolating.

subjecting it to a number of extremely violent chemical tests, measuring its radioactivity qualitatively and quantitatively before and after experiment, to determine whether any change had been effected. It is not altered by passage, mixed with oxygen, over platinum black at the highest attainable temperature, nor by passage over red-hot lead chromate, nor by red-hot magnesium powder, magnesium lime, or zinc dust. Sparking with oxygen over alkali produces no change; neither does ignition of phosphorus in that oxygen. It will combine with no other element under any conditions hitherto employed. The only other gases known which behave in a similar manner are those of the argon series and the thorium emanation. There exists strong evidence, therefore, for the belief that these two emanations are higher members of the argon series.

Dry radium preparations evolve only a small amount of their emanation. The rest is occluded, and decays in that condition; the subsequent products of decay remain mixed with the radium salt. The whole of the emanation can be driven off by dissolving the radium salt in water, and creating a vacuum above the water surface, or a great part by heating the dry salt. Kolowrat has studied the latter subject in detail, using barium chloride containing radium. He finds that from ordinary temperatures up to 350° the amount of emanation given off is constant and only 1 per cent. of the whole; above that temperature it increases rapidly, 90 per cent. being evolved at 830°. The amount then falls to 60 per cent. at 920°, and rises finally to 100 per cent. at the melting point of the salt, about 945°. Similar results were obtained with the fluoride.

He concludes that it is impossible to estimate the radium present in a solid substance by evolution of the emanation unless the substance is fused.

Herchfinkel has found that the amount of occlusion really depends on the physical state of the solid. Thus thorium, didymium, and aluminium salts, containing radium salt, retain scarcely any of the emanation, whereas barium salts retain nearly all. (Since actinium usually occurs with the rare earths, the author concludes that this is the reason why actinium emanation is given off so much more readily than radium emanation, and not any difference between the two emanations.)

Henriot has recently published (1908) the results of a research on the analogous problem of the absorption of emanation by charcoal. At ordinary temperatures it is completely absorbed; at higher temperatures the amount gradually decreases, and by heating the charcoal to dull redness the last traces of emanation are expelled.

Kofler has determined the solubility of the emanation in water and various solutions. The coefficient of absorption—determined by radioactive measurements—in water at 18° is 0·270. The presence of dissolved salts lessens the solubility. Hofman, previously, using similar methods, determined the solubility at the temperatures 0, 20°, 40°, and 60°. The coefficient of absorption was in the respective cases 0·52, 0·28, 0·16, 0·12. It is much larger in such solvents as petroleum and toluol.

The attempts to determine the atomic weight of the emanation have been made by indirect methods. On account of the importance of this figure in connection with Rutherford and Soddy's theory of disintegra-

tion, a special chapter is devoted to these experiments (Chapter VII.).

Radium emanation can be condensed readily by the use of liquid air. Rutherford and Soddy state that the emanation (under an infinitesmally small pressure) condenses to solid or liquid form at about 155°. Henriot has observed that the condensed emanation commences to volatilise between −150° and −160°, at a pressure of only a few millimetres.

It has been mentioned that radioactive disintegrations are accompanied by enormous liberations of energy, chiefly in the form of heat. This is very marked with both radium and radium emanation. P. Curie and Laborde were the first who observed that a radium salt kept itself at a temperature several degrees higher than the surrounding air. They measured the amount of heat in a calorimeter, and calculated that one gram of pure radium chloride emits 100 gram calories per hour. Von Schweidler and Hess have repeated the measurement with greater exactitude, using 1·0523 grams of a radium-barium salt containing 0·7931 gram radium—a relatively large amount. They obtained the figure 118 gram calories per hour per gram radium, which can be accepted as very nearly correct. Rutherford and Barnes have shown that 75 per cent. of the heating effect is due to the emanation and its products. The total heat evolved during the life of a cubic centimetre of the gas is about seven million gram calories, while, when the same volume of electrolytic gas (hydrogen and oxygen in the proportions to form water) is exploded, it gives only 3 gram calories; hence *during its disintegration the emanation*

emits over two million times the amount of heat evolved by the explosion of an equal quantity of electrolytic gas; the latter reaction gives rise to more heat than any other known chemical change.

Ramsay has shown qualitatively in a very interesting manner the production of heat from radium emanation. He took two thermometers, one was an ordinary instrument reading to tenths of a degree; the bulb of the other was hollow. It was standardised against the first and a mixture of hydrogen and emanation was then introduced into the hollow space in the bulb. The two thermometers were wrapped in cotton wool and placed in silvered vacuum vessels; daily readings were taken for three weeks. The difference was 0·52° on the first day, rose to 0·73° on the second, then slowly grew less; the thermometers registered the same temperature at the end of a fortnight.

A further account of work with the emanation is given in the next chapter.

When any substance is exposed to the action of the emanation it becomes coated with an intensely active deposit. This was first observed by M. and Mme. Curie in 1899. It is known as the **active deposit of rapid change**, and has been found to consist of three consecutive products, **Radium A, B, and C.** The whole activity decays to half value in twenty-eight minutes, but the decay curve is very irregular. Studies of the rates of decay of the different rays led to the analysis into three separate elements. All three are soluble in strong acids, and volatile at a white heat. B is volatile certainly below 700°, whereas A and C do not appreciably vola

tilise below 800°; they can be thus partially separated. All three behave as solids in contradistinction to the emanation being immediately deposited on liberation. Radium B is precipitated with barium sulphate, radium C with the copper group.

In 1903 the Curies also observed that substances which have been covered with this active deposit do not lose all their activity after even a prolonged period. Giesel confirmed this. Rutherford found that the activity increases during several years. It is due to the **active deposit of slow change**, which has been resolved similarly into three consecutive products, **Radium D, E, and F.**

Radio-lead (or **Radium D**) was obtained by Hofmann and Strauss in 1901. The lead obtained from pitchblende was strongly and permanently radioactive—hence the name radio-lead. In 1904 Hofmann and co-workers showed that the lead itself is not radioactive, but gives rise to active products separable by chemical means; the inactive lead slowly regains activity. It therefore contains an inactive element of very similar properties which disintegrates slowly into active products. Rutherford has proved fairly conclusively the identity of the rayless parent, the true radio-lead, with radium D, and of the active products with E and F. He found that the activity of the short-life deposit from radium practically vanished after two days; thereafter there was a slow increase during eighteen months. The new activity was due both to α and β particles. Two experiments showed the nature of the changes. A deposit on a platinum wire, after standing for some considerable time, was subjected to the action of heat. Below 1000° it was unaffected.

Between 1000° and 1050° some part volatilised. It no longer gave off α particles, while the β-ray activity decreased rapidly, falling to half value in six days. During the same time α rays were emitted in slowly increasing amounts.

Clean surfaces of metallic bismuth placed for some time in solutions of the slow-change deposit removed 90 per cent. of the substance emitting α particles. The bismuth thereafter emitted these α particles, activity decreasing somewhat slowly; the half-life period was 143 days. The β-ray activity of the solution remained unaltered by this treatment; after the bismuth was taken from the solution the latter commenced slowly to emit α rays.

A simple explanation is given by the assumption of three elements: radium D (rayless); E, giving β rays only; and F, giving α rays only. D is volatile below 1050°; E does not volatilise at that temperature. D is the parent of E, for after it has volatilised the amount of E rapidly becomes less. F volatilises at 1050°, for the wire loses its α activity. It is produced from E, for the α activity of the wire is slowly regained. F, alone of the three, is deposited on bismuth from solutions, and it is the element whose half-life period is 143 days.

Meyer and Schweidler consider that this hypothesis does not completely satisfy the peculiarities of the curve of decay. They suggest a further intermediate product (thus RaE_1 and RaE_2). Radium E_1 possesses properties analogous to those of lead, and is soluble in cold acids, while radium E_2 resembles bismuth in its reactions.

Rutherford has shown the identity of **polonium**, **radio-tellurium**, and radium **F**. Polonium was the first radio-active element discovered by Madame Curie. The sulphide precipitate from acid solutions of pitchblende contained an active substance, which associated itself with bismuth. With this element its properties are so closely allied that it is impossible to effect a complete separation. Madame Curie repeatedly precipitated the nitric acid solution by water. The precipitate contains most of the active material. Marckwald obtained the same substance by dipping a rod of bismuth or antimony in the active solution. These formed an intensely black deposit, chiefly tellurium, and very active; he named the active matter radio-tellurium. Dissolved in hydrochloric acid, all the tellurium was precipitated by hydrazine hydrochloride; the active matter remained in solution. By repeating the process, Marckwald obtained a few milligrams of intensely active material. The production of heat is comparable with that of radium.

There remains the question of the final product. Radium F decays at a moderately rapid rate. What becomes of it? Two lines of argument point to the conclusion that lead is formed. On the assumption that the α particle is helium of atomic weight 4, then, since α particles are given out by radium and four of its products, the atomic weight of the final product should be $226{\cdot}5-(5\times 5=206{\cdot}5$. Lead has the atomic weight 207, a very close agreement.

Again, Boltwood has shown that lead is present in all uranium-radium minerals, and the amount is greatest in the oldest—*i.e.*, those in which the greatest quantity

of uranium has disintegrated. This also points to the fact that the lead is derived from uranium, and therefore from radium.

The Thorium Series.

Thorium was discovered by Berzelius in 1828. It occurs chiefly in Ceylon; the recently discovered mineral thorianite contains more than 70 per cent. of it. It is precipitated from solution by ammonia, and usually separated in the form of oxalate. The metal has been prepared as a grey powder; it volatilises in the electric arc, burns brilliantly in air, and is easily dissolved by warm, dilute acids. The oxide ThO_2 is usually obtained by calcining the oxalate or sulphate. A large number of the salts have been prepared; they are colourless and none are spontaneously phosphorescent (cp. uranium).

Pegram has shown that thorium, like radium, evolves heat, though in much smaller quantity. Pegram and Webb have recently measured the amount evolved from a gram of pure thorium as oxide in equilibrium with all its products. They found the figure $2{\cdot}1 \times 10^{-5}$ gram calories, *i.e.*, one-three millionth of the heating effect of radium.

An account of the disintegration changes of thorium has been given in Chapter II. (pp. 14 *et seq.*). The following additional facts may be noted. Hahn has put forward reasons to suppose that mesothorium can be split up into two elements, which he calls **mesothorium 1**, and **mesothorium 2**. They can be separated by adding zirconium chloride to a solution of mesothorium, and then pre-

cipitating the zirconium with ammonia. Mesothorium 2 is precipitated also, whilst the other remains in solution.

Radiothorium strongly resembles radium in its properties; its activity is several hundred thousand times that of radium; like radium it is precipitated with barium sulphate and has a heating effect of the same order.

The **Emanation** is an inert gas, strongly resembling that of radium. It condenses at −120°. **Thorium A** is volatile above 630°, **thorium B** above 730°; they can in this way be partially separated. They can also be separated electrolytically; thorium B deposits on nickel. **Thorium C** resembles B as far as known.

Rutherford has suggested that the final disintegration product of the thorium series may be **bismuth.**

The Actinium Series.

Actinium was discovered by Debierne in 1899, and independently as *emanium* by Giesel in 1902; it is precipitated with the group of cerium earths, and is closely allied to lanthanum. It itself is inactive; its products have all extremely short lives, so that the maximum activity is quickly reached; this is several thousand times more active than thorium. The two series are very similar, but corresponding members have quite different rates of decay—a sufficient proof of their separate identities. Actinium is precipitated by oxalic acid in acid solution, and the oxalate is insoluble in hydrofluoric acid.

Radioactinium was discovered by Hahn in 1907; at

the same time he succeeded in showing that actinium itself is rayless. Radioactinium gives α rays and corresponds to radium and radiothorium. Giesel has shown its resemblance to the Alkaline earth metals. It can be precipitated from actinium solution by means of finely divided sulphur, by its insolubility in ammonia, or by animal charcoal.

Actinium X was discovered independently in 1905 by Giesel and Godlewski; the separation is similar to that for thorium X. It disintegrates into **Actinium Emanation**, which has a shorter life period than any other known radioactive substance. It was discovered independently by Debierne and Godlewski. The latter showed that Actinium X was its immediate parent. Had it not been a gas, it is improbable that it would ever have been discovered.

The analysis of the active deposit from the emanation was in great part the work of Miss Brooks. Her work led to the recognition of **actinium A** and **actinium B**. Mayer and Schweilder consider that **C** and **D** exist also. Hahn has succeeded in separating **actinium C**.

The Alkaline Metals

Campbell and Wood stated in 1906 that salts of potassium exhibit a radioactivity greater than that of any other substance, except those belonging to the radioactive series. This radioactivity is an inherent property of the potassium, and is proportional to the percentage of potassium in the salt. The salts emit very heterogeneous β rays. Campbell and Wood also found that

rubidium salts are less, but distinctly radioactive, and the rays emitted are much less penetrating than those from potassium. Calcium, sodium, and lithium have, if any, a radioactivity too small to be detected.

McLennan and Kennedy have found wide variations in the activities of different potassium salts, and even of potassium salts of the same composition obtained from different sources; they, however, confirm the result that the radioactivity is inherent in the potassium, and that this element alone of the alkali group has the property in marked degree.

Campbell has repeated and confirmed his results. The activity of the same potassium salt never varies, whatever the source. He finds that the β rays from potassium act on a photographic plate, and are deviated in a magnetic field, while the fastest are slower than those from uranium X.

Henriot and Vavon have attempted to concentrate the radioactivity of the salts of potassium by various fractionations. They failed absolutely, and agree therefore with Campbell and M'Lennan that potassium is inherently radioactive. They confirmed the deviability of the rays in a magnetic field, and their negative charge.

Buchner, using the photographic method, has confirmed the radioactivity of rubidium, but fails to get positive results with potassium, while Levin and Ruer, using the same means, after examining compounds of nearly all the known elements, have found that, with the exception of the elements commonly regarded as radioactive, only potassium and rubidium have an un-

doubted specific activity. Feeble positive results were obtained with antimonic, niobic, and tantalic acids, for which they have not yet accounted.

No theory has so far been put forward to explain the unexpected activity of the elements of the alkali series.

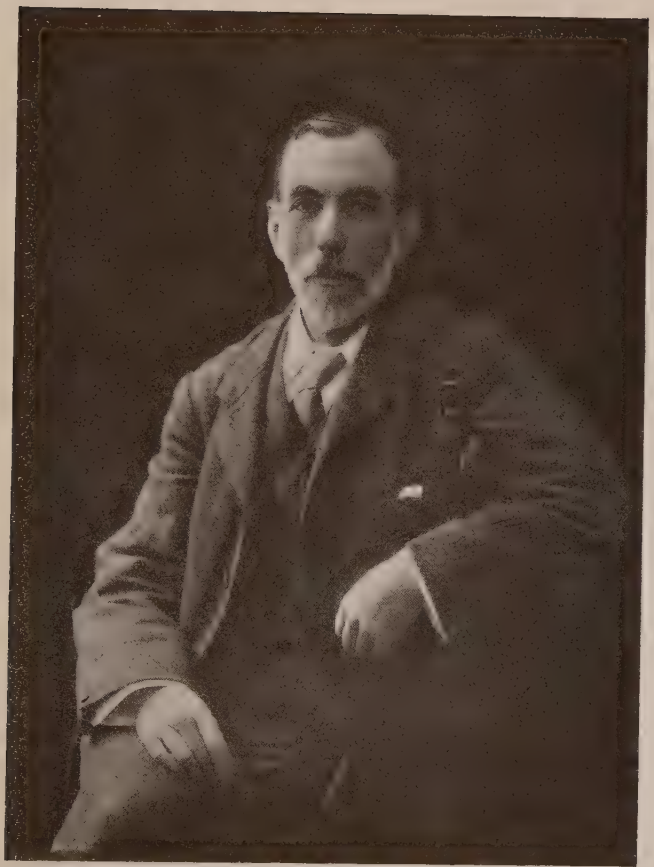
CHAPTER VI

METHODS OF WORK WITH RADIUM EMANATION— THE LIFE PERIOD OF RADIUM

RADIUM emanation has an appreciable life period, 3·86 days, and as it is a gas, it is possible (if sufficient amount of radium is available) to obtain the emanation in quantity large enough to isolate it in a state of purity. As a number of experimenters have quantities of radium approaching half a gram, a considerable amount of work has been carried out with the emanation. The methods employed are based on those devised by Sir William Ramsay for handling very small quantities of gases; as these are typical, a description will be given of the various devices which he has used in his researches on this gas with different co-workers.

It has been mentioned that dry radium salts do not quite yield the whole of their emanation unless fused. Otherwise, the greater proportion remains occluded. On the other hand, if the salts are dissolved in water, and this confined in a space under a vacuum (or strictly speaking, under its own vapour pressure), the emanation is entirely given up into the vacuum and can be pumped away from the solution completely. This means of obtaining it is that commonly employed.

The radium salt is dissolved in water in a small bulb A



Facing p. 60.] [*Photo: Dover Street Studios.*

SIR WILLIAM RAMSAY, K.C.B., F.R.S.,
Professor of Chemistry, University College, London.

(fig. 4), connected through the trap B with the intake tube of a mercury Töpler pump. The tap C prevents the mercury flowing back into the bulb, the trap B catching any that is accidentally allowed to pass the tap. The bulb and tubes are initially pumped empty of air; the mercury is forced past the valve D (by raising the reservoir E sufficiently and closing the outlet tube F) and a little way past C, which is then closed. The mercury seal entirely prevents leakage through C. The emanation is allowed to collect during three or four days, and is then pumped off by repeatedly lowering the reservoir E, opening C for a few seconds, and forcing the gas which passes C through the outlet tube F into the test-tube G, previously filled with, and inverted over, mercury. The operation is continued until a vacuum is produced. The emanation is not present in sufficient quantity to admit of its being pumped away by itself. But both radium salts and emanation decompose water, the property being due probably to the action of the radiations. Hydrogen and oxygen are produced in comparatively large quantity. Ramsay found that as a mean of eight experiments varying from 48 to 336 hours, 32 cubic centimetres of the mixed gases are produced by 1 gram of radium bromide in 100 hours. The quantity from 50 milligrams, 1·6 c.c., can quite easily be passed through the pump without loss. This is the gas which is actually collected in the test-tube; the emanation is carried along with it. There may also be present a very small trace of carbon dioxide.

There is one remarkable feature about the proportions of hydrogen and oxygen in the mixed gases. They never

exactly correspond to those required for the formation of water; there is always some 3 to 10 per cent. of excess hydrogen. This excess has not yet been accounted for completely. Part, perhaps the whole, may be due to the

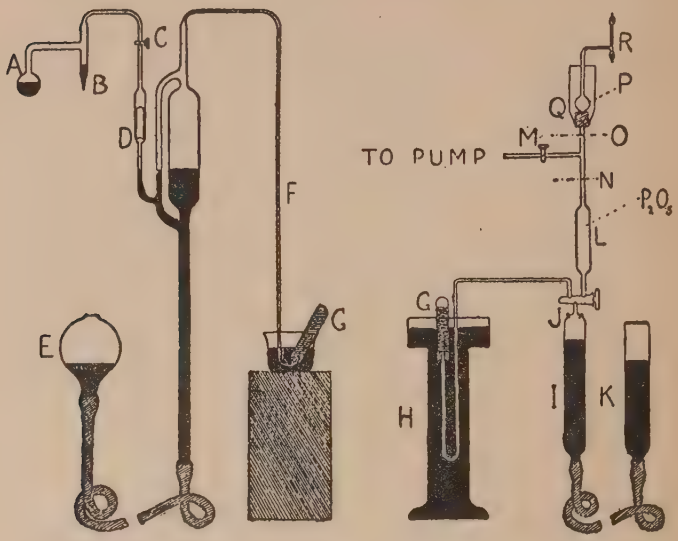


FIG. 4

formation of hydrogen peroxide in the radium solution; this is known to take place to a slight extent. Usher has shown recently that the emanation, acting on tap grease, produces pure hydrogen. This, however, scarcely affords an explanation, as during the operation of pumping the emanation only comes into contact momentarily with the tap grease, which otherwise is protected by the mercury seal. The excess of hydrogen is extremely

useful in enabling the emanation to be separated from admixed gases.

The test-tube G, containing these gases, is transferred to the mercury trough H, and forced through the inverted syphon, made of capillary tubing, and through the three-way tap into the burette I. At the top of the burette a little moist potassium hydroxide has been previously melted to the glass; this absorbs any trace of carbon dioxide. A spark from a coil is passed through the gas by means of the platinum wires at J. Immediate recombination takes place, and only the excess of hydrogen and the emanation remain, but in a moist condition owing to water formed by the explosion. The apparatus above the three-way tap is completely exhausted of air by a second pump, connected through the tap M. This tap is then closed, and the three-way tap opened. The reservoir K is raised and the gas forced through the three-way tap and the small bulb L containing phosphoric anhydride, in order to dry it completely. The mercury is then raised to N, and the three-way tap closed. Liquid air is poured into the cup Q; the bulb P cools quickly to $-185°$, the emanation condensing within, while hydrogen remains gaseous at this temperature. After about five minutes the tap M is opened, and the hydrogen is completely pumped away. It has been found repeatedly that even at $-185°$ the emanation has a slight vapour pressure; pumping must not be carried to excess or else emanation is lost. If the work is carried on in the dark, the pumping is stopped when the bubbles passing down the fall-tube of the pump commence to phosphoresce a little. The tap M is then closed and the

mercury level raised to O to prevent leakage through M. During the whole of this time the cup Q is kept filled with liquid air. After M is closed, the liquid air is allowed to evaporate, whereupon the emanation regains its gaseous condition and can be examined.

Using a somewhat similar method, Ramsay and Soddy succeeded in freeing the emanation from most of its impurities and forcing it into a minute spectrum tube such as R in fig. 4, which was then sealed off and examined. They were unsuccessful in obtaining the spectrum of the emanation; a trace of carbon dioxide masked it. On the other hand, they obtained the spectrum of helium, which rapidly grew brighter. By comparing its intensity with that of other spectrum tubes containing known quantities of helium, they actually succeeded in obtaining an approximate measurement of the amount formed.

Ramsay and Collie, introducing the means already described to free the gas of last traces of carbon dioxide, succeeded in enclosing it in a similar spectrum tube and mapping its spectrum. This is distinct, establishing the emanation as a true element, its general features resemble those of the other gases of the argon series. The appearance is bluish, and not unlike xenon. The visible spectrum shows strong groups of lines in the green and violet. The spectrum was photographed simultaneously by Rutherford and Royds, and Ramsay and Cameron. In the latter case, the spectrum proves to be that of a mixture of emanation and xenon (as was pointed out by Royds). The presence of the xenon here is so far inexplicable. Royds, and later Watson, have rephoto-

graphed the spectrum with a very great degree of accuracy, and their figures show good agreement.

Replacing the spectrum tube by a capillary tube of very fine bore, whose volume measurements were determined subsequently, Ramsay and Soddy made two measurements of the actual amount of emanation produced. They used different capillary tubes and obtained different results in the two cases. In the first experiment there was a sudden large drop during the first day, the contraction thereafter being roughly proportional to the decay of activity. The gas completely disappeared by the end of a month. On heating the tube helium was given off from the walls and detected by its spectrum. They found that the volume of helium was about three times that of the emanation. This agrees with the fact that three α particles are produced before radium D is formed. In the second experiment the initial volume was much smaller. There was no contraction, but the gas expanded during a considerable time.

An attempt to explain these differences was made some years later by Ramsay and Cameron. On account of the *sticktion* of the mercury in its passage through the phosphoric anhydride tube they found it convenient to use a somewhat modified apparatus, a sketch of which is shown in fig. 5. The whole apparatus was arranged by the side of a scale graduated in millimetres. The general arrangement was the same as that shown in fig. 4. A side tube connected with a second reservoir M was introduced; the emanation, having been isolated, was allowed to enter through the tap K, which was closed after forcing mercury through it so as to clear the tube completely of gas. The

gas was forced up into the capillary tube and its volume read at different pressures (by raising and lowering the reservoir M, and noting the difference in the mercury levels). This was repeated daily for some time. Two glass capillary tubes were used, two sets of measurements being taken with each. Their diameters were respectively 0·448 and 0·453 millimetres. For the two final measurements a silica tube of 0·208 millimetres diameter was taken. Silica and glass cannot be joined directly; a ground-in joint was made (at O, fig. 5). Silica tubing possesses several advantages over glass for such measurements. Although the silica tube had less than half the diameter of the glass tubes, yet the *sticktion* of the mercury was negligible, while in the glass tubes it was so great that accurate readings could be obtained only with difficulty. Again, silica is less readily coloured than ordinary glass, pure silicon dioxide being unaffected. The first two capillary tubes were of potash glass, which is so much affected by the β rays that after one or two days the level of the mercury inside can no longer be observed. The effect was partly overcome by confining the emanation to the top

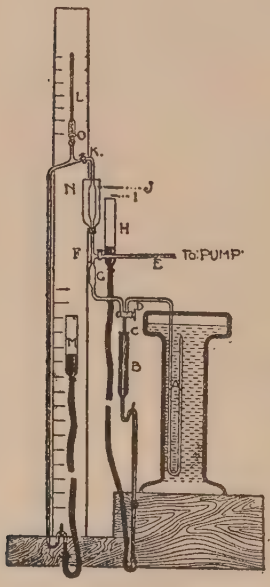


FIG. 5.

of the tubes, except when actual readings were being taken.

The results obtained are here briefly summarised. The observation by Ramsay and Soddy, that the emanation obeyed Boyle's Law, was confirmed by numerous sets of measurements. The divergence of the results in different experiments is due to the nature of the glass capillary employed. The emanation forces a large part of the helium it produces into the walls of the tube. After some time, the disintegration products—radium D especially—appear to act as a shield. The helium is no longer forced into the walls, and the total volume increases. If the glass is unusually impermeable this expansion takes place from the beginning of the experiment, thus showing that the emanation produces more than its own volume of helium.

The life of radium D is so long that at the end of a month, by which time less than 1 per cent. of the emanation remains, scarcely any of the after-products have been formed; while the lives of A, B, and C are of such short duration that they disappear completely within a few hours of their formation. After heating the measuring tubes to remove the colour, an extremely small amount of a brown deposit, possessing a submetallic lustre, has been observed; in all probability this is radium D.

On account of the slight volatility of the emanation at $-185°$ (referred to previously) the experiments showed no very close agreement. The mean of the three which were considered most accurate gave the result that 87·7 milligrams of metallic radium (in solution as bromide)

gave rise in 3·86 days (the half-life period of the emanation according to Sackur) to 0·310 cubic millimetres of emanation. This is the volume occupied by a small pin-head. Ramsay and Soddy's figure for the same quantity of radiation was 0·222 cubic millimetres.

In one of the experiments of Ramsay and Soddy, a very large initial contraction was observed. This was also noticed in four experiments by Ramsay and Cameron. In these, in which the actual initial volumes varied from 0·058 to 0·397 cubic millimetres, the volume contracted in about one and a half hours to 50 per cent., within the limit of experimental error. In two experiments in which continuous readings were obtained at intervals of a few minutes, exponential curves were obtained. On heating the tube, the gas expanded to within 10 per cent. of its original volume. The slow contraction, proportional to the decay of radioactivity, commenced at the end of the rapid contraction. The authors accepted the initial volume as correct, and calculated the life period of radium on this assumption.

The duration of the life of radium has been estimated in two direct ways. Rutherford calculated it originally from an estimation of the number of atoms disintegrating in one second. He found in his early experiments that $6{\cdot}2 \times 10^{-10}$ α particles are expelled per second per gram of radium. From considerations connected with the heat effect he concluded that each atom in disintegrating emits one α particle. Hence $6{\cdot}2 \times 10^{19}$ atoms of radium break up per second. Now it was then considered that one cubic centimetre of hydrogen under normal conditions of temperature and pressure (0° C. and 760 mm.

mercury) contains $3{\cdot}6 \times 10^{19}$ molecules. Hence the number of atoms in one gram of radium, considered as a monatomic gas under the same conditions, can be calculated. If its atomic weight is 226·5 the number is $3{\cdot}6 \times 10^{21}$. In one second therefore the fraction $1{\cdot}95 \times 10^{-11}$ of the total number of radium atoms disintegrates: (in a year, of a gram of radium, about half a milligram has disintegrated). The average life of radium is therefore $1/1{\cdot}95 \times 10^{-11}$ seconds, *i.e.*, 1800 years; its half-life period is 1300 years. Rutherford has recently remeasured the number of atoms expelled per second with much greater accuracy, and his final calculation of the half-life period is 1760 years. His recent experiments are described in Chapter IX (p. 103 *et seq.*).

Ramsay and Soddy used somewhat similar reasoning; they assumed that one atom of radium produces one atom of emanation, and that both as gases are monatomic. Consequently one gram of radium would occupy as gas $(2 \times 11{\cdot}2)/225 = 0{\cdot}1$ litre $= 10^5$ cubic millimetres. From the volume observed in their first experiment *after* the initial contraction, they calculated that one gram of radium produces 3×10^5 cubic millimetres of emanation per second, and consequently the amount changing per second must be $3 \times 10^{-6}/10^5 = 3 \times 10^{-11}$. The average life of radium, the inverse of this quantity in seconds, is therefore 1050 years. In their second experiment they obtained no initial contraction, regarded their initial volume as correct, and by a similar process of reasoning found that the average life was 1250 years. These numbers are of the same order as those found by Rutherford.

The calculation based on the average figure of Ramsay and Cameron gave an average life of 236 years, and even if the volumes after initial contraction were taken, the period became only doubled, and was no longer of the same order as that put forward by Rutherford.

The recent figure of Rutherford and Geiger for the number of α particles expelled from a gram of radium per second is $3{\cdot}4 \times 10^{10}$ (see p. 105). Assuming that the number of atoms of emanation produced are the same, and since the (revised) figure for the number of molecules in a cubic centimetre of any gas under normal conditions is $2{\cdot}72 \times 10^{19}$, it follows that the volume of emanation produced per second per gram of radium is $1{\cdot}25 \times 10^{-9}$ cubic centimetre. The maximum volume, *i.e.*, the volume in equilibrium with its parent, is equal to the rate of production divided by λ (for the meaning of λ see p. 17), which for emanation in seconds is 1/468,000. It is therefore 0·585 cubic millimetre, and the volume per day 0·108 cubic millimetre. This is in marked contrast to the volume per day calculated on Ramsay and Cameron's figures (1·162 cubic millimetres). All these calculations make no assumption as to the atomic weight of the emanation.

Subsequently, in 1908, Rutherford remeasured the volume, employing substantially the same methods. He confirmed the initial rapid change, observing it in nearly all his experiments. But the volumes before and after this change were in no simple and constant ratio, and Rutherford attributed it to the presence of foreign gas (especially carbon dioxide), which was bombarded into

the walls by the emanation, and accepted the final volume as the correct one.

Calculating on this assumption, he obtained in consecutive experiments the figures for the equilibrium amount of emanation per gram of radium 0·59, 0·66, 0·58 cubic millimetre. The mean, 0·61 c.mm., is in very close agreement with his calculated figure. He measured the purity of his emanation by its spectrum, and obtained a correction for the amount pumped away in the course of purification by comparing the γ-ray activity of the two portions.

Debierne, early in 1909, obtained similar results. His method of purification of the emanation is slightly different from Ramsay's. He worked with approximately the same quantity of radium, 0·2 gram, and this was, as usual, in solution. He pumped the emanation away from this solution, and freed it from the accompanying gases in the following manner. Heated copper and copper oxide removed oxygen and hydrogen; phosphorus pentoxide and potash removed water vapour and carbon dioxide, while any nitrogen was absorbed by slightly warmed lithium. The only gases remaining were emanation and helium. The emanation was frozen by immersing the containing vessel in liquid air, and the helium pumped away.

Debierne, like Rutherford, tested the purity of his emanation by observing the spectrum. He confirmed the initial contraction, and took the volume measured *after* contraction as correct. The equilibrium amount of emanation found as a mean of four experiments was 0·58 cubic millimetre, in exact accord with Rutherford's

calculation.* (The actual figures were 0·60, 0·52, 0·61, 0·59 cubic millimetre).

Finally, Ramsay and Gray have measured the volume, and introduced a number of improvements into the original methods, getting rid of all taps, and thus removing one of the chief sources of error. They tested the purity of the emanation by its spectrum, succeeded in totally removing carbon dioxide, the impurity which seems to have given rise to most trouble, and at the same time obtained *pure emanation* which *showed no initial rapid contraction.* They proceeded to study its critical phenomena and an account of these results will be found in the next chapter. Their measurement of the volume of the emanation absolutely confirms the results of Rutherford and Debierne. The equilibrium quantity in three successful experiments was respectively 0·604, 0·606, 0·594 cubic millimetre; the mean is 0·601 cubic millimetre.

The absolute agreement between experiment and theory in these results warrants our acceptance of the assumptions which led to the calculation of the equilibrium figure, from which it follows that *the half-life period of radium is* 1760 *years.*

* Debierne's method of purification suggests a simple means of measuring the quantity of helium and emanation together, from which the rate of production of helium could be calculated. It would be interesting to see if this agreed with that obtained by Dewar (p. 103).

CHAPTER VII.

THE ATOMIC WEIGHT OF THE EMANATIONS. LIQUID AND SOLID RADIUM EMANATION

For reasons which will be discussed later the atomic weight of radium emanation is perhaps at the present time the most important constant of the radioactive elements. The Rutherford and Soddy theory of disintegration may require to be modified largely should this constant be 176, the figure supported by recent research, instead of 222, the figure required by the theory in its present form. It is therefore of considerable interest to consider the researches so far completed and the stress which can be laid on them.

The standard method of determining the atomic weight of a gas of the argon series, which forms no compound with any other element, is by means of a determination of its density. Up to the present time the very small volume of the emanation which can be isolated (resulting from the, in reality, very small amounts of radium available) has not permitted this method to be adopted, though we may expect confidently that it will be utilised at an early period, in view of the increasing delicacy of methods of weighing invented in recent years.

The methods employed so far have been indirect. A great number of diffusion experiments have been made

by different observers with varying results. Ramsay and Gray determined in 1909 the critical data, and by comparing these with the other gases of the argon series, have shown that there is strong probability that the figure 176 is the correct one.

Diffusion Methods.

It is well known that if two gases are allowed to diffuse into one another, their rates of diffusion are inversely proportional to the square roots of their molecular weights. For example, an elementary experiment consists in allowing hydrogen and carbon dioxide to diffuse under equal pressures through a tiny aperture into air. It is found that equal volumes diffuse through the aperture in times roughly as $\sqrt{44}$: $\sqrt{2}$ *i.e.* in accordance with the law enunciated (*Graham's law*).

The method can be employed in consequence to determine the molecular weight of a gas, by the inverse process. It was first used for radium emanation by Rutherford and Miss Brooks in 1901. Their method consisted in dividing a metal cylinder into two equal parts by a movable metal slide, and introducing a considerable amount of emanation into one. Each part contained an insulated brass rod connected with a sensitive electrometer, while the cylinder itself was charged to 300 volts. by connection with a battery. Suitable precautions were taken to prevent the setting up of convection currents by heating effects. The slide was withdrawn, and the rate of diffusion of the emanation into the second half

of the cylinder was measured by the change of its electrical effects on the two electrometers. From this its rate of diffusion into air, and the consequent molecular weight could be calculated. The minimum figure for the coefficient of diffusion k* into air, which the authors considered as nearest the truth was 0·07, while that of carbon dioxide is 0·142. The molecular weight of carbon dioxide is 44, and this multiplied by $\left(\frac{0\cdot142}{0\cdot07}\right)^2$ is very nearly 176.

P. Curie and Danne in 1903 used a slightly different method; they connected a closed vessel charged with emanation to air through a capillary, and measured the rate at which the emanation diffused through the capillary. From this they calculated k to be 0·100. In their experiments they found that the emanation obeys all the ordinary laws of diffusion, dividing itself between two vessels placed in connection proportionately to their volumes and temperatures. This agreement with the behaviour of ordinary gases allows the greater stress to be laid on the conclusions based on such results.

Bumstead and Wheeler in 1904 directly compared carbon dioxide and radium emanation by allowing them to diffuse through a porous plate. Their results led them to expect a molecular weight of about 180.

Makower, using a method based on the divergence of rate of diffusion of different gases from the strict law,

* The coefficient of diffusion of one gas into another is inversely proportioned to the square root of the product of their molecular weights. Air is taken as unity.

found a value in the neighbourhood of 100 (1905), while Chaumont, who has most recently worked on the subject, finds a value for k of 0·1015, giving a molecular weight even smaller (1909).

As all the qualitative tests to which it has been exposed point to the conclusion that the emanation is a gas of the argon series, its atomic weight must be equal to its molecular weight, like those of the remaining members, and all the experiments quoted support the contention that the atomic weight is in the neighbourhood of 176.

This experimental result is liable to objection on two grounds. In the first place, the emanation in these experiments has been compared with gases of much lower molecular weight. Graham's law is only *approximately* true, and if the law does not hold strictly, we must expect that the error must be exaggerated considerably by such a comparison. Makower's method of correction, however, as we have seen, led to an even lower figure. The second ground of criticism lies in the fact that here a monomolecular gas has been compared with gases which are not monomolecular; this also introduces a possible source of serious error.

Neither objection applies to the experimental work of Perkins, whose results were published in 1908. He compared the diffusion of the emanation with mercury vapour, a monomolecular gas, at, necessarily, a comparatively high temperature. All the previous experiments had at least shown that the emanation possesses a very high molecular weight, and Perkins attempted especially to find if this was greater or less than that of mercury, 200. He found that it was distinctly greater. On

account of the importance of his results, I include a slight account of his method.

The diffusion vessel consisted of an iron cylinder, through the closed ends of which passed a second, placed concentrically. In the middle of the inner cylinder were bored numerous small holes each of one millimetre diameter, and closed with plugs of asbestos, which was found to be suitable. The whole apparatus was heated either to 250° or 275° by placing it in an electric furnace. Mercury in small quantity was introduced into the outer vessels, and mercury vapour commenced to diffuse through the plugs into the inner cylinder. Through this a slight but continuous current of hydrogen was passed, which carried on the mercury vapour through a cooler receiver, where it condensed, and could be collected and weighed from time to time. When liquid mercury no longer remained in the outer cylinder, the amount of vapour diffusing out obeyed *the same exponential law* as did a limited quantity of emanation confined in the outer cylinder under the same conditions. *The amount diffusing out in any given time always was a fixed and constant proportion of the total amount remaining.*

Measurements with mercury vapour and with emanation were therefore directly comparable. In the experiments with emanation it was collected with the accompanying hydrogen over a water reservoir, and measured by the amount of radium C deposited in a given time on a negative electrode placed in it.

In the actual experiments observations with mercury vapour and emanation alternated, in order to get rid of

errors arising from changes in the porous plugs. The following were the mean results obtained.

Coefficient of diffusion k for mercury vapour at 250° (mean of 4 experiments) 0·0370.

Coefficient of diffusion k for emanation at 250° (mean of 6 experiments) 0·0341.

Coefficient of diffusion k for mercury vapour at 275° (mean of 3 experiments) 0·0407.

Coefficient of diffusion k for emanation at 275° (mean of 2 experiments) 0·0376.

Since all the conditions were the same direct comparison was possible at each temperature.

Hence at 250° the molecular weights of the emanation is $\frac{200 \times 0{\cdot}0370^2}{0{\cdot}0341^2} = 235$

and at 275° the molecular weight of the emanation is $\frac{200 \times 0{\cdot}0407^2}{0{\cdot}0376^2} = 234.$

Perkins claims that his results show distinctly that the emanation has a higher atomic weight than 200. The only criticism which it seems possible to put forward on these experiments, is that, as the emanation was collected over water, in which it is fairly soluble, a certain portion must have dissolved in each experiment. This would result in k being smaller than the real value, and the measured atomic weight too large.

Diffusion methods applied to the emanations of thorium and actinium are rendered more difficult, especially with the latter, by reason of the much shorter life period of these gases, and in consequence even less stress can be laid on the results. Using somewhat modified methods, to suit the special difficulties of the

short period, Rutherford found the value $k = 0{\cdot}09$ for the thorium emanation. Makower compared radium and thorium emanations directly, and found that their diffusion rates are approximately equal, showing that their molecular weights must also be very nearly the same.

Debierne has measured k for actinium and finds it 0·112, while Bruhat, using his method, obtained the same figure. Russ recently compared directly the emanations of thorium and actinium, and concludes that their molecular weights are as 1·42 to 1, where thorium is heavier.

So far as diffusion experiments tell us, therefore, we can conclude that the emanations of radium and thorium have nearly equal atomic weights, while that of actinium is distinctly lower. We are able to lay considerable stress on the direct comparison results, since the emanations are probably all monatomic and of high molecular weight. Their deviations from Graham's law should therefore be of the same nature. It must not be forgotten, however, that the experimental error in the case of actinium is by far the greatest.

Liquifaction and Solidification of Radium Emanation—its Critical Constants.

Early in 1909 Rutherford succeeded in condensing the emanation into liquid by forcing it into a very fine capillary tube, cooled to a low temperature. He found that its boiling point was 208° absolute (- 65°C.) and that the liquid was practically colourless, although producing

a most marked greenish phosphorescence. At a still lower temperature, a reddish to orange coloured patch was noted, which Rutherford attributed to the solid emanation. He found the liquid produced 500 times its volume of gas, which corresponded to a density not less than five, if the atomic weight were 222.

These results were confirmed almost immediately by Ramsay and Gray. They find that the boiling point is $-62°$ C. or 210° absolute, a figure in close agreement with that of Rutherford; the melting point is $-71°$ C., while the critical temperature is 104·5° or 377 absolute. They find as the mean of six observations that one cubic millimetre of liquid yields 555 cubic millimetres of solid. As they have pointed out, this gives no clue to its molecular weight. The density of the liquid can be found only by assuming the density of the gas. If the latter is 176 that of the liquid is 4·6, if 219, then 5·7. They give the following account of the properties of the liquid and solid. "The liquid emanation is colourless and transparent like water, when seen by transmitted light; it itself is, however, phosphorescent, and shines with a colour varying with the nature of the glass forming the tube in which it is confined; it might be more correct to say that it causes the glass to phosphoresce. The colour varies from blue to lilac; in silica it is blue; in lead-potash glass bluish green; and in soda glass lilac; when compressed strongly in soda glass, the colour reminds one of the cyanogen flame, at once blue and pink. On cooling further the liquid solidifies, and ceases to transmit light. . . . The solid glows with great brilliancy, like a small, steel blue, arc light. Further

reduction of temperature changes the colour to yellow, and in liquid air it is brilliant orange-red; the colour change takes place in inverse order on warming. The red phosphorescence disappears pretty sharply at - 118°."

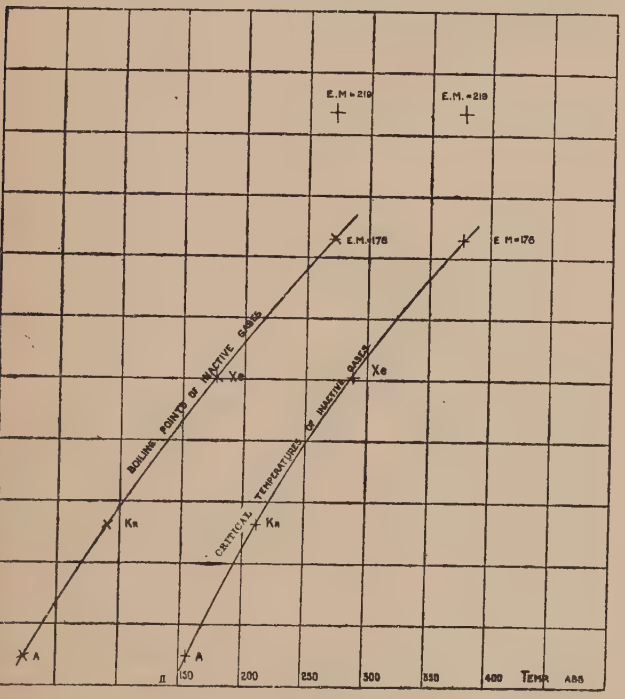


FIG. 6.

The authors utilised their results to determine the atomic weight of the emanation, by comparing them with the corresponding figures for argon, krypton and xenon, in which series the emanation is included by universal consent. The results are shown in figures

6 and 7. The boiling points, critical temperatures, and critical pressures are plotted against the atomic weights. The curve obtained for argon, krypton, and xenon in each case cuts the ordinate for the emanation figure at atomic weight 176.

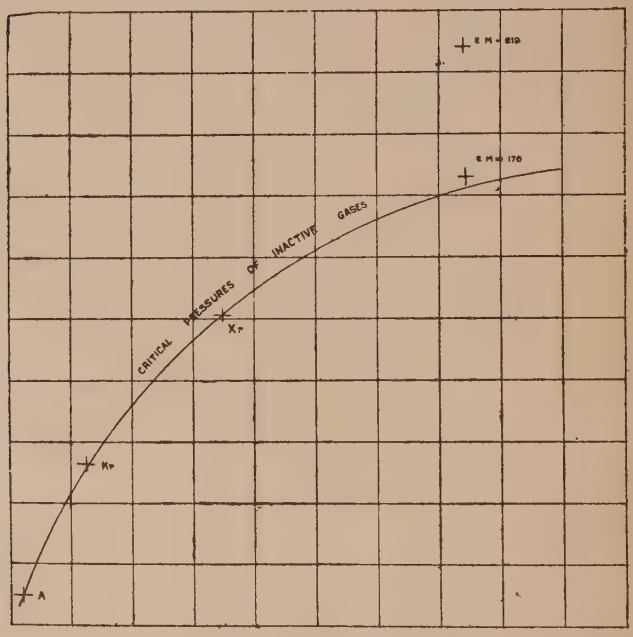


Fig. 7.

The figure 219, obtained by calculating the difference in the complete vertical series of the periodic table, and applying the average to the argon series, is distinctly too high. The only criticism of this result which it is possible to put forward (provided the initial assumption of a continuous curve is correct), is that the temperature

curves, on which greater stress is laid, are nearly straight lines, so that slight errors in the figures for krypton or xenon might affect the curves materially.

There remains, then, a considerable discrepancy in the experimental results. All the early diffusion methods, and the recent work of Ramsay and Gray, point to an atomic weight of 176. The most accurate diffusion experiments, those of Perkins, give an atomic weight of about 230.

CHAPTER VIII

THE CHEMICAL EFFECTS PRODUCED BY THE RADIATIONS

THERE is reason to believe that the chemical effects produced by radioactive elements are all due to the radiations which they emit, and that the difference in the effects produced by α and β rays is quantitative only. Most of the experiments have been made with radium or its emanation, but it must be remembered that it is probable that all the elements which emit rays would produce the same effect if the action of these rays could be concentrated sufficiently.

The possible chemical actions of the radiations are of two kinds. They can, and do bring about chemical actions on the molecules. It seems not unlikely that they can also cause the disruption of the atoms themselves. In this chapter I shall only deal with examples of the first kind.

Giesel was the first to observe that radium salts decompose the water in which they are dissolved. Davis and Edwards have noted a rapid combination of hydrogen and oxygen, when solid radium salt is actually placed in the mixed gases. Ramsay obtained a similar effect by adding emanation to electrolytic gas. When the radium salt is placed in a closed glass bulb, and this immersed

in the liquid or gas under observation, any action which takes place must be due to β and γ rays only—derived from radium B and C—for all the α rays are absorbed by the glass envelope. Under such conditions Ramsay found no decomposition of water; Jorissen and Ringer observed no combination between hydrogen and oxygen.

Most of the early work was carried out with radium enclosed in glass tubes, in which case the effect was certainly due to β rays. The results of such experiments may be summarised briefly. Becquerel has shown that yellow phosphorus changes into the red modification, while mercuric chloride, in presence of oxalic acid, undergoes reduction. Hardy and Wilcocks have found that iodine is liberated from iodoform. The former has noticed that globulin is coagulated; Dryer and Hanssen state that of a large number of proteins examined, only vitellin is coagulated. Jorissen and Ringer have shown that hydrogen and chlorine combine slowly; Berthelot has proved that iodine is liberated from iodic acid, though not to such an extent as from iodoform. Nitric acid is decomposed. Creighton and Mackenzie have published an account of their research on hydriodic acid, in which they show that β rays increase the rate of decomposition. If the β rays are absorbed, the γ rays remaining produce a greater effect, but neither light nor β rays produces any effect in absence of oxygen.

The action of α and β rays on glass and precious stones with production of colour changes and phosphorescence has been dealt with sufficiently in Chapter III.

The Curies observed that oxygen is converted into ozone. The statement has been repeatedly confirmed.

A small quantity of hydrogen peroxide is produced in water containing dissolved emanation (Ramsay and Cameron).

Ramsay has noticed that dry oxgyen in contact with mercury attacks it when emanation is present. Moist oxygen does not. The phenomenon is, no doubt, connected with the formation of ozone.

Ramsay and Cameron published in 1908 a detailed account of the action of radium emanation on water and on certain gases. The apparatus was a modification of that shown in fig. 5; the capillary tube L was replaced by a measuring tube such as those shown in fig. 8, *a* and *b*.

The emanation, along with excess of hydrogen, was separated from the radium bromide solution as previously described. With the liquid or gas on which its action was to be tested, it was frozen solid at $-185°$ in the bulb J, by means of liquid air; the excess of hydrogen was pumped away. An alternative method was to add the emanation directly to the pure gas under observation, along with hydrogen or oxygen, according as one or other of these was among the products of the reaction. The apparatus was modified by the removal of the phosphorus pentoxide tube where water, or gases reacting with phosphorus pentoxide, were to be treated.

In all cases, by raising the reservoir H, the gases were forced through the apparatus, past the stopcock K, into a measuring tube, as in fig. 8, *a*. This contained a piece of blue glass, sealed to the tube, and broken off at a very fine point A, to which the mercury surface was accurately adjusted by raising or lowering the reservoir M (fig. 5). The difference in height between the mercury surface at

A and that in the reservoir, subtracted from the barometric pressure, gave after the necessary temperature corrections the pressure exerted at 0° by the perfectly definite volume of gas enclosed. Readings of the pressure were taken daily. In each the tap was opened, the mercury readjusted to the point A, and the tap then closed, so that the gas was kept at constant volume throughout the experiment. By calibrating the measuring tube with mercury at the end of the experiment, the capacity was found. The observed pressures then gave the actual volume of gas at 0° and 760 millimetres pressure, at each time of observation.

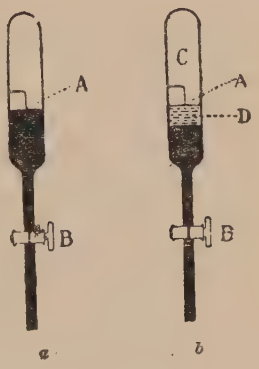


FIG. 8.

After three or four weeks, the amount of emanation remaining was practically negligible; by this time also the pressure became constant within the limit of error. When water and gas were both present the point A was set to the surface of the water as in fig. 8, *b*. In this way, while the tap B was closed, the gas and water phases, C and D, were both kept at constant volume. There is considerable reason to believe that emanation decomposes in different media at the same rate. If it obeys Henry's law, it will divide itself in a certain ratio between the gas and water phases, and this ratio will remain unaltered during the whole of the experiment. The emanation in each phase will produce its own effect.

The difference in the two effects is the volume change measured.

As each experiment lasted a month, means were devised to subdivide the emanation and the gas containing it, and carry on several experiments simultaneously. In this way a number of interesting results were obtained. The qualitative results may be first summarised. Several experiments confirmed the rapid decomposition of water, and recombination of hydrogen and oxygen. Hydrochloric acid is decomposed into hydrogen and chlorine; mercury absorbed the chlorine, forming a deposit of mercurous chloride. Ammonia was decomposed into nitrogen and hydrogen, and these gases recombined; the amount of recombination (measured by absorbing the ammonia with calcium chloride) was smaller for the same quantity of emanation than of the decomposition.

In two experiments with carbon dioxide, there was a slight contraction of volume, due apparently to the action of oxygen—a product of the decomposition—on mercury, while a ring of carbon was deposited in appreciable quantity above the mercury surface. In a third experiment an attempt was made to absorb the oxygen with yellow phosphorus as fast as it was set free, but the phosphorus was immediately converted into the red variety. In this case, too, there was slight but steady increase in volume, and the gas finally contained a small quantity of oxygen mixed with a comparatively large quantity of carbon monoxide.

Starting with pure carbon monoxide, the pressure steadily decreased, and the deposit of carbon was appreciable. The gas at the end of the experiment con-

tained both oxygen and carbon dioxide. It would therefore appear that with both oxides of carbon all possible reactions take place.

An extremely curious result was obtained with a mixture of steam and hydrogen jacketed at 130°. No

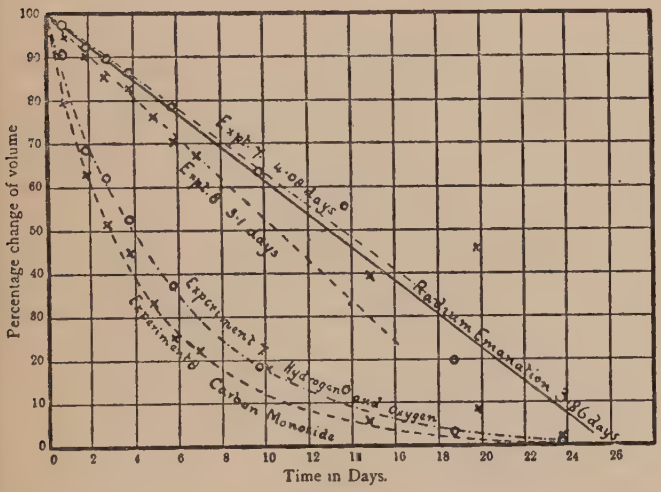


FIG. 9.

decomposition (which would be indicated by an increase in pressure) was observed during six hours. This is the only experiment in which no change was observed*; with water the change is immediately noticeable. Hydrogen and oxygen combine appreciably at 130°.

It has been shown in Chapter II. that all radioactive

* Cameron has repeated this experiment and has found that the steam actually is decomposed.

elements decompose according to the law expressed by the exponential equation

$$\frac{v_o}{v^t} = e^{-\lambda t} \quad . \quad . \quad . \quad (1),$$

where v_o is the original amount (volume, if a gas) v_t that at time t, and λ is constant for the particular element (0·1795 for radium emanation if time is reckoned in days). It was also shown that, although all the elements have an infinite life, yet their half-life period is quite definite; and, as has already been mentioned, Sackur's value for the emanation is 3·86 days.

The chemical action induced by radium emanation obeys the same law. Thus, if V_o is the initial volume of gas under observation, V_t the volume at time t, and V_∞ the final volume, then

$$\frac{V_o - V_\infty}{V_t - V_\infty} = \frac{v_o}{v^t} = e^{-\lambda t} \quad . \quad . \quad . \quad (2).$$

The curves in fig. 9 show the values for $(V - V)_\infty$ plotted against time, taking $(V_o - V_\infty)$ as 100, and the corresponding logarithmic values together with the logarithmic curves for radium emanation. These all give points lying on straight lines, and the curves closely resemble those for the decomposition of the emanation itself. These examples can be taken as typical.

The following table shows the period of half decay, and the values for λ. In the case of experiments 5—7, the measuring tube contained phosphorus pentoxide to absorb the water as fast as it was formed.

No. of Expt.	Reaction.	Total pressure change.	Volume change.	Half-time.	λ	Amount of Emanation	V_E
1.	$2H_2O \rightleftarrows 2H_2+O_2$	459·5 mm.	0·766 c.c.	3·35 days	0·207	0·081 E	9·46 c.c.
2.	Do.	84·7 ,,	0·390 ,,	3·47 ,,	0·200	0·062 E	6·29 ,,
3.	$2H_2+O_2 \rightleftarrows 2H_2O$	232·5 ,,	0·688 ,,	3·40 ,,	0·204	0·093 E	7·18 ,,
4.	Do.	60·2 ,,	0·221 ,,	4·37 ,,	0·159	0·025 E	8·84 ,,
5.	$2H_2+O_2 \rightleftarrows 2H_2O$	84·3 ,,	0·555 ,,	4·08 ,,	0·170	0·044 E	12·61 ,,
6.	Do.	124·8 ,,	0·526 ,,	4·30 ,,	0·161	0·105 E	5·01 ,,
7.	Do.	229·6 ,,	0·476 ,,	4·08 ,,	0·170	0·063 E	7·56 ,,
8.	$\begin{cases} 2CO=2C+O_2 \\ 2CO=CO_2+C \end{cases}$	49·5 ,,	0·177 ,,	3·10 ,,	..	0·049 E	—
9.	$N_2+3H_2 \rightleftarrows 2NH_3$	76·5 ,,	0·232 ,,	3·17 ,,	—	0·239 E	0·97 ,,
10.	$2NH_3 \rightleftarrows N_2+3H_2$	76·9 ,,	0·427 ,,	(1·4) ,,	—	0·230 E	1·86) ,,
11.	$2HCl \rightleftarrows H_2+Cl_2$	—	0·538 ,,	(5·9) ,,	—	0·069 E	(7·30) ,,

In most cases the total pressure change was small. A slight error of the final readings—due to leakage or any other cause—materially affects the half time as determined from the curve. In view of these facts the truth of equation (2) must be held as established.

The authors point out that it follows from this that the amount of chemical action taking place in any time is strictly proportional to the amount of emanation which decays in that time. From this it can be deduced that other conditions being the same, *each atom of emanation, as it disintegrates, produces a certain definite chemical effect.*

In the seventh column are given the amounts of emanation used in each experiment, calculated on the assumption that E is the quantity of emanation obtained from one gram of radium (as metal) dissolved in water, in 3·86 days. The eighth column shows the total volume change which E c.c. of emanation would effect. In experiments 5—7 the conditions were similar; the effect of E varies from 5·01—12·61 c.c. gas combined. It follows therefore that some other factor besides the

amount of emanation present determines the total amount of chemical action. In all probability there is a surface effect; but the present data do not allow its determination. Since in any single experiment the surface remained constant throughout the experiment, no error from surface effect affected the time of half change, but it prevents the determination of the actual volume of the gas decomposed in the water phase in the first two experiments. In both, the water phase was much less in volume than the gas phase; the action on water appears to be much greater, volume for volume, than on the mixture of gases.

The two final experiments show considerable difference from the theoretical values. In the case of ammonia these were due possibly to traces of air in the ammonia, with resulting production of water; this would immediately saturate itself with the gas. The final analysis of the gas pointed, however, to a marked deficiency in the quantity of hydrogen.

Usher has recently repeated and confirmed the results with ammonia and with nitrogen and hydrogen, although he finds that the recombination in the mixed gases is extremely small. He has explained the too small quantity of hydrogen found analytically by showing that it is bombarded into the wall of the containing glass vessel in considerable quantity by the emanation, in such large quantity, in fact, that it can be liberated afterwards by heating the powdered glass *in vacuo*. His results with ammonia also afford a possible explanation of the difference in the figures obtained with dry hydrogen and oxygen by the previous observers. He finds that

the emanation exerts a maximum efficiency, a maximum chemical effect, when it is diluted to the greatest extent in the gas on which it is acting, so that if equal quantities of emanation are allowed to act on two quantities of the same gas, one of which is twice the volume of the other, the emanation will produce the greater effect on the first.

Ramsay has carried out numerous experiments on the quantitative production of hydrogen and oxgyen by radium salts dissolved in water (see p. 61). Debierne has obtained similar figures with both radium and actinium solutions.

In all the previous experiments the action is due to the combined effect of α and β rays.

Debierne has recently published results, in which he shows that β rays alone can certainly decompose water. His apparatus consists of a U-tube containing water and sealed to a manometer, after the space above the U-tube had been exhausted of gas. The radium salt was placed between the limbs of the U-tube so that the rays had to traverse two thicknesses of glass. The whole was enclosed in a thick lead vessel. The arrangement is sketched in figure 10. The decomposition of the water was registered by a rise in pressure in the manometer.

By a somewhat similar method, Kernbaum has studied the same decomposition more completely, subjecting water to the effect of β rays, ultraviolet, light and X-rays. He finds that X-rays produce no measureable effect (and it can therefore be concluded that the same holds for γ rays. Compare, however, the results of Creighton and Mackenzie).

Ultraviolet light (*i.e.*, electrons) decomposes water to produce hydrogen and hydrogen peroxide, while his quantitative results with the β rays from radium suggest that the reaction is represented by the equation

$$2H_2O = H_2 + H_2O_2$$

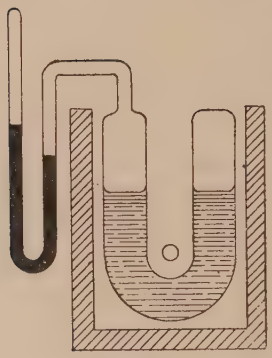


Fig. 10

Again Herchfinkel has just shown that the decomposition of carbon dioxide can be effected either by ultraviolet or by β rays, and Cameron has proved that hydrogen and oxygen are recombined by β rays.

It seems, therefore, that most of the reactions which can be brought about by α and β rays together, (as in the cases where emanation is mixed with gases or dissolved in liquids), are also produced by the β rays alone. It is consequently of interest to see what is the relative chemical effect of the two kinds of radiations. Some preliminary measurement with water by Cameron point to the conclusion that α and β rays produce ray for ray in liquids a quantitative effect of the same order.

Two possible mechanisms of these chemical effects suggest themselves. One, a theory of collision, would be similar to that of the production of ions in a gas. We should then expect that the relative chemical effects of the two rays would be proportional to the relative ionis-

ing effect, about 100:1 (α rays greater). This cannot be the case in liquids, although it is not disproved for gases. The other apparent possibility is an effect of the nature of electrolysis, and here the similarity observed in the magnitudes of the effects might possibly prove more easy of explanation.

CHAPTER IX

THE PRODUCTION OF HELIUM DURING RADIOACTIVE CHANGES, AND ITS IDENTITY WITH THE α PARTICLE

THE importance of the spectroscope in radioactive work is second only to that of the electroscope and electrometer, used in the specialised radioactive methods. The principle of the instrument may be recalled in a few words. It has been known for a very long time that when a beam of white light is passed through a prism of glass or quartz, the light is refracted, bent in the passage, and is, moreover, broken up into its constituent parts, giving a *visible spectrum*, in which red is least bent, and then in order yellow, orange, green, blue, and violet, which is the most refracted of all. The *invisible* spectrum continues on either side, giving on the one hand the *infra-red*, on the other the *ultraviolet*. Ordinary white light consists of the mixed light waves of a great many elements in a state of incandescence in the sun, and it is because of this that the whole spectrum from red to violet is almost completely filled up. If a single element is heated to incandescent, as for example in the ordinary analytical method in a Bunsen flame, a spectrum of only a few, sometimes only one, definite line is observed. Thus sodium is distinguished by one very strong yellow line, potassium by a red line, and one far in the blue, and hydrogen has several in which one red line predominates.

These lines are definite, and none is given by more than one element, (although sometimes the difference between two lines of two elements is so minute that it cannot be discerned by our present methods). The presence of a particular line, therefore, indicates the presence of the corresponding element, and this method of detection is extraordinarily delicate. A mixture of elements can be identified as easily as a single one, provided each has a definite spectrum, and is present in quantity sufficient to prevent its being masked by the spectra of the others. The lines are standardised according to their wave length, which is perfectly definite for each light ray or spectral line; the ultraviolet rays have the shortest wave lengths, the infra-red the longest.

In observing the spectra of gases, these are sealed in spectrum tubes, glass or quartz, which consist usually of a straight capillary, to each end of which is joined a wider tube, containing an electrode of aluminium or some suitable metal welded to a platinum wire; the latter is sealed through the glass, and in this way the two electrodes can be connected with a supply of electricity of high voltage. The enclosed gas is usually at a pressure of two or three millimetres of mercury. It has been mentioned in Chapter I. that under such conditions a broad glow fills the tube. It is concentrated in the capillary portion, emitting a strong light, which in the case of hydrogen is pink-red, of neon brick-red, of helium electric blue. This light, examined through the spectroscope, gives the characteristic spectra of the gases present.

Mention has been made already of the change of radium

emanation into helium, predicted by Rutherford and Soddy, and actually observed by Ramsay and Soddy. The apparatus employed was in great part similar to that shown in fig. 4, p. 62. The initial observation, of which an account was published in 1903, was made with the gases evolved from 20 milligrams of pure radium bromide, dissolved in water. The hydrogen and oxygen were removed by contact with a red-hot spiral of copper wire, partially oxidised, and the resulting water vapour by a tube of phosphorus pentoxide. The remaining gas was forced into a small spectrum tube connected with a U-tube. It showed the spectrum of carbon dioxide; but on cooling the U-tube in liquid air most of the carbon dioxide condensed, and the yellow line (D_3) of helium became visible in the spectrum. This was conclusively identified.

A second experiment with 30 milligrams of bromide gave a better result; the carbon dioxide was removed completely, and most of the lines in the helium spectrum were observed. Several further experiments were carried out with similar results.

Attempts were made, which have already been described (p. 65), to measure the volume of the emanation. The capillary tube used for measurement had a very fine platinum electrode fused in at the upper end. As the gas was confined over mercury, the capillary itself could be used as a spectrum tube. In this experiment the emanation was condensed at liquid air temperature, and the hydrogen and any helium pumped off (see p. 63). After a series of measurements had been made during twenty-eight days, a scarcely visible amount of gas re-

mained. On passing a spark and freezing out the mercury vapour, the helium spectrum was visible.

This experiment proved conclusively that helium is a product of the disintegration of radium emanation. Whether it is produced directly from radium itself can only be ascertained when the relative volumes produced from radium and emanation together, and from emanation alone, have been accurately determined.

The change of radium emanation into helium has been confirmed by numerous observers. Since this is perhaps the most striking of all the transformations, some account is given of their work.

In nearly all cases the spectrum was observed with a direct vision spectroscope. The eye-piece was adjustable by means of a micrometer screw, which could be read to the hundredth part of a millimetre. The spectroscope was either standardised previously by observing a series of known spectra, or else the spectrum of the suspected gas could be observed simultaneously by means of a comparison prism. In the former case a convenient method is to use a tube containing hydrogen, helium, and mercury vapour,* which give a number of strong lines throughout the visible spectrum. By plotting the measured screw-readings of these lines against their known wave-lengths, a curve is obtained, from which the wave-length corresponding to any particular measurement can be determined accurately to one or two Ångstrom units.

P. Curie and Dewar, in 1904, confirmed the production

* This method is due to Collie.

of helium in the following manner: About 0·4 gram of radium bromide was placed in a small quartz bulb joined to a quartz tube, and the whole connected with a mercury pump. After evacuation the radium salt was heated till fusion and the whole again evacuated. The quartz bulb and tube were then sealed off. Twenty days later Deslandres examined the spectrum of the gas contained in the tube, using external electrodes. He observed the entire spectrum of helium, and no other lines, although a current was passed through the tube for three hours.

Indrikson carried out an experiment with the gases from 10 milligrams of bromide placed in a vacuum tube, which was then sealed off. He stated that after fourteen days he observed the red, green, blue, and violet lines of the helium spectrum, although the yellow line was absent. Such a conjunction seems unlikely; Himstedt and Meyer consider it probable that the lines observed belonged to the secondary spectrum of hydrogen.

These physicists carried out, in 1904-5, a series of most exhaustive tests; the results of their work supplied any final proof, if that were required. In their first experiment 50 milligrams of radium bromide were placed in a U-shaped glass tube, to which was joined a vacuum tube containing aluminium electrodes. The tubes were joined to a pump, and the whole apparatus completely evacuated during seventy-two hours. The tubes were then sealed off. Initially only the spectrum of hydrogen and carbon monoxide were visible. After fourteen months the yellow and green helium lines were seen, but could not be photographed. Three months later most

of the strong helium lines were visible. The tubes employed in this, and in most of Himstedt and Meyer's experiments, were comparatively large, which probably accounts for the length of time before sufficient helium had accumulated to give a visible spectrum.

The authors considered it unlikely that the helium could come from the electrodes, but carried out two experiments to test this point specifically. Twenty-five milligrams of the bromide were placed in a small U-tube, to which was joined a small spectrum tube. The whole was connected to a pump, evacuated, and washed out with hydrogen ten times, and during each operation the current was passed to remove completely any helium from the electrodes. Finally, the tubes were exhausted completely and sealed off. After three months the helium spectrum was definitely identified.

The remaining 25 milligrams of bromide were converted into sulphate, and this dried and ignited. It was then placed in a tube of quartz, to which a small electrodeless tube was joined with marine glue. The tubes were connected to a pump, evacuated, and rinsed with hydrogen as usual, and finally sealed off. A Tesla coil was used to light up the spectrum tube. After three weeks the four principal helium lines were observed, and two weeks later they were identified conclusively.

Later, the same workers carried out a series of negative tests; in all cases the results were satisfactory.

Giesel performed somewhat similar experiments, and also confirmed the production of helium.

In view of these numerous experiments by different workers, all leading to the same result, the change of radium through its emanation into helium must be regarded as finally proved. It is of interest to see what other radioactive substances produce helium.

Debierne, in 1905, repeated Ramsay and Soddy's work with about 10 milligrams of radium bromide. His methods were very similar,* and he obtained the same results in numerous experiments carried out during a period of six months. He then substituted very active actinium salts for the radium bromide. A solution of actinium chloride disengaged hydrogen and oxygen in quantity comparable as regards activity with that from a radium salt solution. Treating the gases in the usual way, he succeeded in identifying the helium spectrum visually and photographically. After specially purifying his solution from radium, he still obtained the same results; helium was also observed in the gas produced by heating some dry actinium fluoride. Debierne states that the quantity of helium formed is in all cases comparable with that derived from radium of the same degree of activity. He checked his results by carrying out blank experiments with other gases, especially electrolytic gas; helium was never observed.

In 1907, Giesel, using the methods he had employed for radium salts with a strongly active actinium preparation, succeeded in identifying the D_3 line of helium.

Ramsay has obtained some indications of the forma-

* Compare p. 71.

Facing p. 103.]

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tion of helium from thorium solutions, but this cannot yet be regarded as proved. In this connection Strutt's work on thorium minerals, which will be dealt with in Chapter XI., is of great importance.

Greinacher and Kernbaum have carried out observations during eleven months with polonium (radium F) preparations enclosed in evacuated spectrum tubes of small capacity. No trace of helium was observed.

Hofmann and Wölff state that when radio-lead, or radium D sulphate is placed in a completely exhausted capillary tube, after several months the yellow, green, and blue helium lines become visible, although all attempts with radium E and F have given negative results.

Since 1907 Soddy has been carrying out a series of experiments, in which he has attempted to prove directly the formation of helium from uranium and thorium. His results are positive. The actual amount observed was extremely small, but of an order of magnitude to be expected from the theory of disintegration.

Dewar, in 1908, actually measured the amount of helium produced from radium, by observing its effect on a radiometer in a M'Leod gauge. He used the 70 milligrams of radium chloride purified by Thorpe for his atomic weight determination, (see p. 46), and from the results of two experiments calculated that the rate of production of helium per day, per gram of radium was respectively 0·42 and 0·31 cubic millimetres, giving the mean 0·37.

It is now time to give some account of the work of Rutherford and his co-workers on the actual identification of the α particle with helium. Thomson has

measured the electric charge e carried by a charged molecule, or ion of gas, and found it to be $3{\cdot}4 \times 10^{-10}$. Assuming that this was the charge carried by an α particle Rutherford measured the total charge of the α particles expelled from a thin film of radium salt in a given time. He calculated from this that $6{\cdot}2 \times 10^{10}$ α particles are expelled per second from one gram of radium, and four times as many from one gram of radium in equilibrium

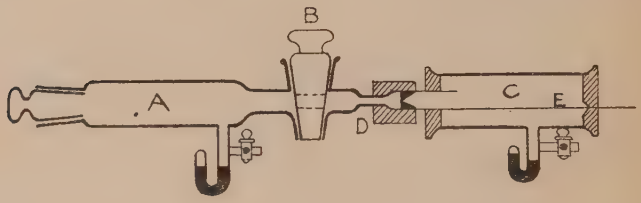

FIG. 11.

with its products. If the charge carried by the α particle was $2e$, then the total number would be halved. To settle this point he carried out experiments in which he actually numbered the α particles expelled.

Townsend has shown that the electric effect of the radiations can be magnified automatically several thousand times by the ionic collision continually producing fresh ions; the most favourable conditions are obtained in gases at a pressure of only a few millimetres of mercury. This phenomenon enabled Rutherford and Geiger to carry out the following experiments successfully.

A small quantity of radium was placed in the vessel A, (figure 11) at some distance from the stopcock B. The vessel was completely evacuated. Through the stopcock

it was placed in communication with the second vessel C; the two spaces were separated only by a very thin sheet of mica at D, so thin that it would cut off but a small proportion of the α particles which came in contact with it. In the vessel C the pressure was only a few millimetres of mercury; it contained the charged wire E, insulated through the vulcanite stoppers connected with an electrometer. On opening the stopcock, a certain number of α particles reached the mica, passed through it, and the ionisation set up was recorded on the electrometer. If the radium C was placed at a sufficiently great distance from the mica plate, only a limited number of the α particles passed through. The experiments were so arranged that ten or eleven particles per minute were recorded, each by a sudden oscillation of the electrometer mirror. The actual number varied and the variations agreed with those calculated from the theory of probability, and from this also was reckoned what proportion of the total number emitted would reach the mica plate. From the actual number counted, the total number emitted was found. The total number expelled by radium in equilibrium with its products is $3{\cdot}4 \times 10^{10} \times 4$ per second per gram of radium (*i.e.*, each gives rise to $3{\cdot}4 \times 10^{10}$).

This figure was confirmed by counting the number of scintillations produced by bombardment of zinc-sulphate with α particles, and it was found that each α particle produces one scintillation.

Rutherford and Geiger next proceeded to remeasure E, the charge carried by an α particle, and found it to be $9{\cdot}3 \times 10^{-10}$ electrostatic units. They give reasons for be-

lieving that the previous measurements of e by Thomson and others are too small, and that e, the charge carried by a hydrogen atom, should be $4{\cdot}65 \times 10^{-10}$ electrostatic unit, half the value of E.

Reasoning from these data, the following interesting results are obtained:—

The *atomic weight* of the α particle is 3·84. That of helium is 3·96, strong evidence that the α particle is helium (plus the two electric charges).

Volume of the emanation. *See* p. 70.

Rate of production of helium. The number of α particles produced per gram of radium in equilibrium is $4 \times 3{\cdot}4 \times 10^{-10}$. The volume of helium formed per gram of radium is, therefore, since there are $2{\cdot}72 \times 10^{19}$ molecules in any gas under normal conditions, $5{\cdot}0 \times 10^{-9}$ c.c. per second = 0·43 cubic millimetre per day, or 158 cubic millimetre per year. This is in close agreement with the figure found by Dewar (p. 103).

Life of radium deducted from the proved rate of change, 1760 years (compare pp. 68-72).

Finally, Rutherford and Royds have succeeded in actually firing α particles through glass into a vacuum in sufficient quantity to demonstrate that helium was the resulting product. The apparatus shown in fig. 12 was used. The glass tube A, in which emanation was confined, was less than 1/100 millimetre thick, and as this is equal to only 2 centimetres of air in stopping power for α particles, while their range in air varies from 3·5 c.ms. (radium) to 7·08 c.ms. (radium C), the majority of the particles must have penetrated into the vacuum

T, surrounding A. The small vacuum tube V was attached to T, so that on running up the mercury, the spectrum of any gas which had been projected into the vacuum might be examined. After six days the distinguishing lines of helium were clearly discernible. The only remaining possibility other than that the α particle was a charged atom of helium, was that the helium had *diffused* through the glass (Jacquerod's experiments have shown that helium diffuses easily through quartz at high temperatures, while an experiment by Ramsay and Cameron suggests that this can also take place at ordinary temperatures with some kinds of quartz). This was disproved by replacing the emanation in A by helium; none diffused through, and no helium spectrum was seen. On pumping out the helium and replacing it by fresh emanation, the spectrum of helium was again seen after several days.

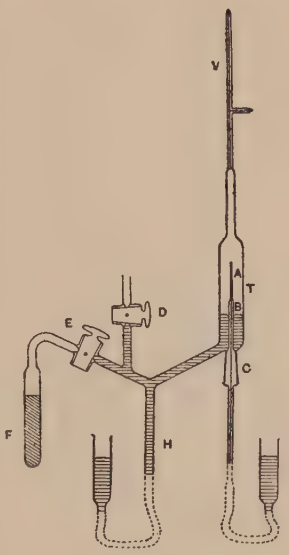

FIG. 12.

All these lines of argument have definitely established the fact that *the α particle is a helium atom with two positive charges of electricity.*

The total quantity of helium produced during these

radioactive changes is of an order which, when considered in connection with the total amount of radioactive changes taking place, lends support to the suggestion that all the helium in the earth's atmosphere has been produced by such transformations. The questions must at once arise: are these transformations limited to the production of helium? can no other gases of the argon series be produced in this way?

CHAPTER X

RECENT ATTEMPTS AT TRANSMUTATION

THE alchemistic doctrine of transmutation was accepted by most thinkers until the beginning of the sixteenth century. The modern definition of an element is due to Boyle, and scarcely can be said to have received wide acceptance by the end of that century. His predecessors put forward some form or other of the *elements* of the ancients, of which the Aristotelian system—earth, air, fire, and water—is typical. Such elements were in reality *properties*, which each substance possessed in different degrees. With such conceptions a belief in transmutation might easily arise, since if two *substances* consisted of different proportions of these *elements*, they should be capable of transformation into one another by altering the proportions.

The belief in transmutation arose at a very early date; attempts to transmute base metals into gold or silver date to the Egyptian era. (The name χημεία, given to this art, is possibly derived from *chémi*, an old name for Egypt). Superficial observations of a nature easy to comprehend led to these attempts. Thus iron utensils left in copper mines were coated with a deposit of copper from the accumulated waters; copper could be changed

into white or yellow alloys by admixture with various earths. The transformations into copper, and into silver or gold, were apparent.

The early history of chemistry is largely the history of such attempts at transmutation, with various discoveries incident thereon. As chemical knowledge grew, the evidence of these changes became more and more capable of disproof, and belief in them was only upheld by deception and self-deception.

With the acceptance of Boyle's definition of an element, the belief in transmutation in great part vanished. Dalton's hypothesis of definite indivisible atoms peculiar to each element made it appear still less likely. Not until the development of the subject of radioactivity, and in particular till Ramsay and Soddy showed that radium is transformed into helium, could any support be given to the belief.

It is desirable at this stage to distinguish between the terms "transformation" and "transmutation." The element-changes so far dealt with, which take place in nature under normal conditions, are examples of *transformation*. *Transmutation* contains the idea of active human intervention, and it is convenient to ascribe it to changes so brought about where they differ from those which would have occurred without such intervention.

The old and new ideas of transmutation differ greatly. The alchemist sought to transmute large quantities of material, and made the attempt for personal gain. The modern chemist knows that such transmutations, if possible, can only be carried out in extremely small quantity, by the expenditure in some form or other of a

relatively enormous amount of energy. The product of transmutation will be probably of less value than the original element. Thus the idea of gain is eliminated, and the study of these changes can have no commercial application.

The most convenient source of a relatively enormous amount of energy, which can be set free locally, and allowed to act on the molecules and even the atoms of different substances, is unquestionably radium emanation. The enormous store of energy liberated as each particle disintegrates has been mentioned. When this is liberated in water, the water is decomposed; an account of this, and of the effect on various gases, has been given in Chapter VIII. p. 84. The changes there discussed are molecular. It is now necessary to consider what proofs have been put forward for atomic emanation produced by this agency.

From the fact that radium emanation decomposes water into hydrogen and oxygen, Sir William Ramsay was led to try its effect on a solution of copper sulphate, with the idea that there would result a deposit of copper equivalent to the hydrogen. That such an idea was justifiable is proved by his results with silver solutions, as yet uncompleted, in which a deposit of silver is actually formed, while oxygen is liberated, along with only a very small quantity of hydrogen. In the case of the copper solution, however, no copper was deposited, but on analysing the solution a trace of lithium was observed spectroscopically. Such a result was quite unlooked for. The copper sulphate was prepared from the ordinary pure salt, recrystallised four times. Laboratory copper

sulphate invariably contains lithium, but it has been found that after such a series of crystallisations, the lithium is entirely eliminated.

The experiment was repeated several times. On the second occasion copper sulphate was prepared from pure copper electrolytically deposited on platinum and "contact" sulphuric acid. The copper sulphide from this experiment was converted into acetylide, and that into nitrate; this was employed in a third experiment.

In all cases a trace of lithium was found after treatment with emanation. This lithium might result in four ways—(*a*) as impurity in the copper salt, (*b*) from the glass bulb in which the experiment was carried out, set free either by action of the emanation or of the salt solution, (*c*) as impurity in the reagents used in analysis or from the vessels employed, or (*d*) as a transmutation product from one of the elements present, in which case, since the same results were obtained with both nitrate and sulphate, the probable parent substance would be copper.

To test these possibilities Ramsay and Cameron carried out a series of three experiments as carefully as possible.

(1) Pure copper nitrate solution was treated with emanation in a glass bulb. After treatment the solution was analysed. Lithium was present.

(2) A roughly equal quantity of the same solution was placed in a bulb of the same glass, sealed up, and allowed to stand along with the first. No lithium was found.

(3) Pure water was placed in a similar glass bulb, and treated with emanation. Afterwards it was evaporated

to dryness and the residue tested. No lithium was found.

The further results obtained in these experiments will be discussed presently.

Since no lithium was found in the second experiment (*a*) was ruled out. The results of the second and third experiments together negative (*b*). Since the " treated " and " untreated " solutions were analysed in identically the same way, hypothesis (*c*) seems extremely unlikely, so that an actual transmutation would seem to have taken place.

Some account of the methods used in these experiments will be given, since these are the typical of all the later work in this direction.

(*a*) *Preparation of copper nitrate.*—Pure laboratory copper sulphate was dissolved in extremely pure water (the water used throughout these experiments was of such degree of purity that 20 c.c. gave a totally unweighable residue); the solution was electrolysed and the copper deposited on a rotating cathode of smooth platinum. After washing with pure water about half the copper was dissolved in a few cubic centimetres of redistilled nitric acid of such degree of purity that 50 c.c. gave a residue of less than 0·4 milligram. The solution was evaporated to dryness on the water-bath, and heated for some time to expel nitric acid. It was dissolved in pure water and filtered into two glass bulbs newly made from the same piece of tubing. The first was treated with several accumulations of emanation. It was finally sealed off and the emanation allowed to decay. The second was exhausted and sealed.

(*b*) *Method of treatment with emanation.*—The original plan has been modified slightly to allow the substitution of silica for glass bulbs. It will be described in its present form. The apparatus is shown in fig. 13.

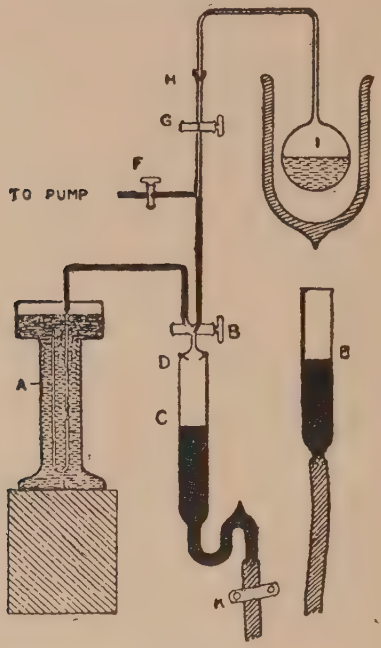

FIG. 13.

The bulb I is, if of silica, joined to the rest of the apparatus by means of a ground silica-glass joint at H; if of glass, it is directly joined at H. The bulb is half filled with the solution which is to undergo treatment, by means of a second side tube, not shown in the figure; this is then sealed off. The whole apparatus is evacu-

ated. The emanation, and hydrogen and oxygen, obtained from radium bromide solution in the manner already explained (p. 60), are transferred as usual through the inverted siphon A into the burette C, and there exploded; the excess of hydrogen and the emanation are admitted to the bulb. This is then cooled to $-185°$ by means of liquid air, and the hydrogen pumped off as completely as possible through the tap F. Mercury is allowed to rise just above the ground joint H, and acts as a seal, preventing any leakage. In most cases more than one *dose* of emanation is added. The additions are made in a similar manner, at intervals of three or four days In each case the gases formed since the last addition are previously pumped off as completely as possible and stored. The total quantity of gas is analysed at the end of the experiment [see p. 116 (*d*)], and the solution also analysed.

(*c*) *Method of analysis of the solutions.*—In each case the copper nitrate solution was transferred to a platinum crucible, and saturated with sulphuretted hydrogen passed through a platinum tube. The sulphide precipitate was separated by centrifugalisation in a silica tube, and the filtrate evaporated to dryness and ignited. The residue was treated with a few drops of pure water, and the solution, which should contain all the alkali salts, was evaporated, ignited, weighed, and examined spectroscopically. The whole of the analysis was carried out in either silica or platinum vessels.

In both experiments calcium and sodium (strong) were present. Lithium was present in the "treated" case only. The weight of the alkali residue was different

in the two cases: that from the "treated" solution was distinctly larger. This would lead to the assumption that sodium is also a transmutation product (but further evidence has shown that no stress can be laid on these weight relations). The treatment of the pure water in the third experiment has been indicated already.

(*d*) *Method of analysis of the gaseous products.*—The methods employed for determining the amounts of the ordinary constituents of a gas mixture were those devised by Ramsay himself. They are applicable to quantities as small as one or two cubic centimetres, the results in such cases being accurate to within 1 per cent. The actual measurements are carried out in a gas burette provided with a series of points sealed to the glass, similar to those shown in fig. 8, p. 87, and the measurements are made in a similar manner, the pressure exerted by the gas being measured, from which its volume can be calculated. (The calibrated gas volume is that from the tap to a mercury-point surface.)

In the gas-mixtures dealt with, the constituents are, as a rule, only hydrogen, oxygen, the oxides of carbon, nitrogen, and inert gases. The total volume is first measured. The gas is then forced back through the inverted siphon into a test-tube and allowed to remain for a few minutes in contact with moist potash. After again measuring a spark is passed; if necessary oxygen is added, and the mixture again exploded. The gas is treated with potash for the second time; the contraction in this case is due to carbon monoxide. From these series of measurements the amounts of hydrogen, oxygen, and the oxides of carbon are easily calculated. Finally,

the gas is transferred to a second test-tube containing a pellet of phosphorus, and the excess of oxygen thus removed by warming the phosphorus. The residue consists of nitrogen and inert gases.

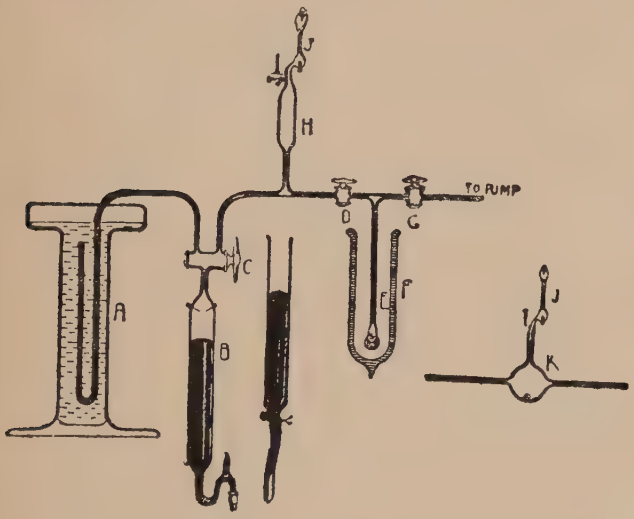

FIG. 14.

In examining these, advantage is taken of the fact, discovered by Dewar, that charcoal cooled to the temperature of liquid air absorbs nitrogen and the heavier inert gases. Neon and helium are not absorbed. It is thus possible to separate them from nitrogen and argon. The separation is carried out in the apparatus shown in fig. 14. The gases are taken through the inverted siphon into the burette B, the rest of the apparatus is evacuated through the tap G connected to a mercury pump. During this operation the bulb E containing charcoal is heated at

230° in quinoline vapour to free the charcoal from absorbed gases, and at the same time a current is passed through the spectrum tube J to remove hydrogen and any other gas from the electrodes. G is then closed. The stopcock C is opened and the gas allowed to enter the apparatus; to prevent leakage mercury is raised above the stopcock, which is then closed. E is cooled in liquid air, and the charcoal absorbs any nitrogen and argon (also krypton and xenon) present. The tube H is surrounded by a paper cup, moistened with water; on filling this with liquid air a vessel of ice is produced, in which the liquid air evaporates comparatively slowly. The object of this precaution is to prevent loss of helium and neon through their contraction to small volume in the cold region E. D is then closed and mercury forced up through C to the point I. The spectrum can then be examined, and, if desirable, the spectrum tube sealed off.

The stopcock G is next opened, the charcoal again heated to 230°, and the gas pumped off and collected in a test-tube over mercury. Oxygen is added to it, and sparks from an induction coil are passed through the mixture for some hours; a small quantity of potassium hydroxide absorbs all the oxides of nitrogen formed. The residue, oxygen and inert gases (minus helium and neon) are then admitted to an apparatus similar to that just described, but without the charcoal bulb, containing instead phosphorus in a bulb K to absorb the oxygen. After this has taken place, mercury forces any gas that remains into the small spectrum tube, and its spectrum can be examined.

The three experiments of which mention has been

made gave the following results. From the " untreated " copper nitrate no gas could be pumped off, as of course was expected. The " treated " water gave hydrogen, oxygen, traces of the oxides of carbon, and a small quantity of nitrogen. The experiment with copper nitrate gave a small quantity of nitric oxide (observed by the formation of red fumes during admixture of the portions of gas pumped off before each addition of emanation). There were also present hydrogen, oxygen, and small quantities of carbon dioxide and nitrogen.

The inert gas from the experiment with pure water consisted almost entirely of neon. Initially the spectrum tube gave the blazing red colour of neon, tinged slightly heliotrope owing to the presence of a small quantity of helium. Only the red, yellow, and green lines of helium were visible; the blue and violet lines were not observed.

In the gases from the copper solution no neon or helium was observed, but argon only. The trace of nitrogen present in this case would perhaps account for the argon, but the absence of helium, which is not easily masked by argon, suggests a possibility that some part at least of the argon was derived from the emanation.

In August 1908, Mme. Curie and Mlle. Gleditsch published an account of experiments devised especially to test the supposed copper-lithium transmutation. They found that when pure water was allowed to stand in contact with glass, or silica, the dissolved salts contained lithium. On this account the whole of their work was carried out in platinum vessels. They used a solution of copper sulphate fractionally recrystallised a large number of times to free it from lithium. The quantities

of copper sulphate and of radium emanation were comparable with those used in Ramsay and Cameron's experiments. No lithium was detected in the solution after treatment; moreover the weights of the alkali residues from "treated" and "untreated" solutions did not differ distinctly. The authors conclude that the transformation of copper into lithium cannot be held as established.

The two series of experiments would appear to have been carried out in a perfectly parallel way; the only explanation that permits them to be homologated is that in those of Ramsay and Cameron, any lithium in the glass was undissolved by copper sulphate solution (as actually shown) unless emanation was present.

Perman tried the direct action of α particles on solid copper nitrate by placing opposite each other *in vacuo* silica dishes containing, one, a film of that salt, and the other a film of a barium radium salt.

In another experiment he evaporated together some gold chloride and some radium barium chloride. In neither case did he get any production of lithium. He used extremely small quantities of radium in these experiments.

Cameron has since shown that the alkaline residues from "treated" and "untreated" silver nitrate solution show no difference in weight exceeding the limit of error, and from these results and those of Curie and Gleditsch it can be held as established that it is useless to seek for "weighable" transmutations with the quantities of emanation at present at our disposal.

Soddy and Mackenzie found that traces of helium and

neon can always be obtained from aluminium electrodes, which have been used previously with these gases, and even with fresh electrodes. Strutt has observed that it is possible to detect the neon from one-tenth of a cubic centimetre of air. These results suggest the possibility that the neon obtained in the experiments of Ramsay and Cameron was due to an accidental trace of air through leakage, or possibly came from the electrodes. The latter supposition is extremely unlikely, as other experiments with the same electrodes gave no neon.

Rutherford and Royds have tested the former possibility by repeating the experiments, taking elaborate precautions to exclude air. In five experiments with radium emanation and water they obtained neon only in one instance, and in this case they proved that there was accidental air leakage. Incidentally, they confirmed Strutt's figure, and proved that it is possible, with great precautions, to observe the neon spectrum from one-fifteenth of a cubic centimetre of air. As this gas exists in the air in one part in one hundred thousand, it is therefore *possible to detect one fifteen-hundredth of a cubic millimetre of neon* spectroscopically.

Taking all these data into consideration, there is good ground for doubting the production of neon from the emanation under conditions so far realised. The use of the spectroscope has resulted, therefore, in only one definite proof of transformation, that of the production of helium, or as we now know of an α particle, which loses its electric charge and becomes helium.

The measurement of minute quantities of gases pro-

bably ranks next as an accurate method of detection to the spectroscope. With great care, using small apparatus, the presence of 0·01 cubic centimetre of, say, carbon dioxide, can be detected with certainty. This volume weighs 0·02 milligram. Using a microbalance, quantities of solid of not more than one or two milligrams can be weighed with an accuracy of one part in a thousand. But such quantities are too small for experimental work of the nature described above. Where changes of weight are concerned in which an ordinary balance must be employed, the utmost degree of accuracy attainable is just over 0·02 milligram. Where the substances or solutions must be put through several chemical operations, the degree of accuracy becomes proportionately less.

Gas measurements and methods of identification suggest a delicacy great enough to distinguish possible transmutations. And here we have the recent work by Ramsay on thorium and similar elements.

He commenced with an endeavour to find out if helium were a product of the disintegration of thorium. This has been referred to already (p. 102). A series of experiments with pure thorium nitrate were commenced in December 1905, and lasted more than three years. 270 grams of this material were dissolved in about 300 cubic centimetres of water, in a round bottomed flask of approximately twice that capacity. The flask was joined to a capillary tube, closed by a good tap. The whole was connected to a Töpler pump and evacuated, then the tap closed, the flask disconnected from the pump, and inverted in water so that the solution acted as a trap

to prevent leakage. In no case did any leakage, even of water, take place at the tap. The latter, had it occurred, could have been distinguished by the very marked difference of the refractive indices of the concentrated solution and the water. After some time the flask was reconnected to the pump, the gases formed pumped off, and analysed by the methods already indicated, and the apparatus sealed as before and allowed to stand over another interval. In the initial experiment carbon dioxide was not looked for. The gases, on their way to the pump, were passed through a U-tube surrounded by liquid air, and a small quantity of white solid condensed. This was suspected to be carbon dioxide. In the last experiment, as an additional precaution, the tap was sealed with mercury. The mercury apparently acted as a catalyst, as a vastly greater quantity of gas was given off. The carbon dioxide was fractioned from it, by condensing the gases at liquid air temperatures, but the figure below can only be considered a minimum.

A control experiment was made with 300 grams of mercuric nitrate—a good oxidising agent—dissolved in a minimum quantity of water under similar conditions. A summary of all the results follows:—

Solution	Duration of Experiment	CO_2	Electrolytic Gas ($2H_2+O_2$)	N_2	TOTAL
$Th(NO_3)_4$	168 days	suspected	0·061 c.c.	—	3·523 c.c.
,,	250 ,,	0·588 c.c.	0·017 ,,	5·145 c.c.	5·750 ,,
,,	173 ,,	1·08 ,,	0·02 ,,	1·64 ,,	2·74 ,,
,,	228 ,,	1·209 ,,	0·016 ,,	1·321 ,,	2·546 ,,
,, (with Hg trap)	315 ,,	0·622 ,,	—	—	180* ,,
$Hg(NO_3)_2$	228 ,,	0·015 ,,	0·034 ,,	3·628 ,,	3·677 ,,

* Almost pure nitrogen.

In considering these figures it is seen that after each experiment with thorium there was a considerable quantity of carbon dioxide present, which must have accumulated somewhere in the preceding interval; in the experiment with mercuric nitrate the amount was negligible, and gives an idea of what might arise from presence of organic matter, or previous condensation on the vessel walls. The total amount of gas in the first four experiments appears to fall off distinctly, calculated for equal times of accumulation, whereas the amount of carbon dioxide increases appreciably. Had it arisen from the two sources suggested above, or from a trace of carbonate in the nitrate, we should expect the rate of production to decrease during the three years. The non-presence of a corresponding amount of hydrogen to account for the oxygen of the dioxide, is easily explained on the assumption of a certain amount of reduction of nitrate to nitrite. Similar results were obtained in the experiments with copper nitrate, where the reduction even went the length of the production of nitric oxide.

There appear some grounds from these experiments to consider that an actual degradation of thorium into the lowest member of its series, carbon, has taken place. Accordingly, Ramsay and Usher attempted to hasten the process by treating the thorium, and similar elements (in solutions of their salts) with radium emanation. If the original degradation really existed, it was not the normal degradation accompanied by the production of an α particle, and the next degradation product, but an abnormal degradation due, perhaps, to bombardment of thorium atoms by the α particles. This effect could

therefore be increased by increasing the number of α particles. This is brought about most readily by "dosing" with radium emanation.

The results of their experiments are shown on the following table. The general method of treatment was that described on p. 114.

Solution	Volume of Emanation Employed	N_2	O_2	CO_2	CO	$(2H_2+O_2)$	H_2
		c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
$Th(NO_3)_4$	0·1120 c.mm.	3·686	—	0·551	—	—	—
,,	0·0765 ,,	0·639	—	0·124	—	—	—
$Zr(NO_3)_4$	0·0692 ,,	0·762	—	0·116	0·008	—	—
,,	0·0865 ,,	0·456	—	0·124	0·002	—	—
$Pb(ClO_3)_2$	0·0649 ,,	2·655	—	0·007	0·006	2·531	—
$Ti(SO_4)_2$	0·0912 ,,	0·210	—	0·054	0·096	—	0·69
H_2SiF_6	0·0724 ,,	—	—	0·063	—	9·15	1·03

The authors calculated the weights of carbon dioxide corresponding in each case to one cubic millimetre of emanation.

Solution of	$Th(NO_3)_4$		$Zr(NO_3)_4$		$Pb(ClO_3)_2$	$Ti(SO_4)_2$	H_2SiF_6
	I.	II.	I.	II.			
CO_2	2·93	0·968	1·071	0·873	0·102	0·982	0·518 mgm

They draw the conclusion that all the members of the carbon series yield carbon under the action of the emanation. The amounts increase the higher the atomic weight of the element, and they consider it probable that this is due to the greater instability of the heavier atoms.

In all their experiments appreciable quantities of nitrous gases were produced and these had to be removed before analysis by shaking up with mercury. This supports the argument already put forward to explain the

absence of hydrogen in these and the previous set of experiments.

Transformations occurring in nature through long periods of time would lead to the accumulation of much larger amounts of products; these should be detectable by ordinary analytical methods, and this method of attacking the problems of transformation is dealt with in the next chapter.

CHAPTER XI

CHEMICAL EVIDENCES OF TRANSFORMATION

It has been pointed out in Chapter II. p. 16 that when one radioactive element disintegrates into a second, and the life of the latter is shorter than that of the first, then ultimately a state of equilibrium is reached, in which the quantity of the second element disintegrating in any given time is equal to the amount formed in that time. Under such conditions, provided the life of the parent element is great in comparison, so that its amount is practically constant, then the amounts of the two in any mineral containing them must be in a definite ratio. This holds true even if the intermediate products occur, provided that their life is sufficiently short to permit the state of equilibrium to be reached. Uranium and radium give a good example of such a fixed ratio.

Again, the ultimate disintegration product—of course a non-radioactive element—will accumulate in ever-increasing amount as the parent substance, and the mineral containing it, grow older. Consequently the amount of this product in any mineral must depend on the age of the mineral. Lead is supposed to be the ultimate disintegration product of the uranium-radium series.

The evidence put forward to support these statements will now be considered.

The method employed to estimate the amount of

radium in a mineral has been gradually evolved from those used by Boltwood and Strutt. A known weight of the mineral is decomposed with acids, and the solution boiled to expel accumulated emanation completely. It is then kept in a closed vessel, and the emanation allowed to accumulate for a known period. The solution is again boiled, the emanation removed, and measured by the usual radioactive methods. From the amount of emanation formed in a given time the amount of radium can be calculated. If thorium or actinium be present in the mineral, then its emanation will also be present. By observing the initial rate of decay of the mixed emanations, the relative amounts of the thorium and radium emanations can be determined. Actinium emanation decays so rapidly that it can scarcely be detected in such a mixture unless present in relatively large amount. The amounts of thorium and uranium present in minerals are determined by the usual methods of chemical analysis, though Strutt has found it convenient and accurate to estimate the thorium from the amount of its emanation.

The following figures are taken from a much larger table published by Boltwood in 1905; the emanation equivalent is given in arbitrary units:

Mineral	Locality	Emanation equivalent of radium in 1 gram of mineral	Weight in grams of uranium in 1 gram of mineral	Ra : Ur
Uraninite	N. Carolina	170·0	0·7465	228
,,	Joachimsthal	139·6	0·6174	226
,,	Saxony	115·6	0·5064	228
Uranoplane	N. Carolina	113·5	0·4984	228
Carnotite	Colorado	49·7	0·2261	220
Orangite	Norway	23·1	0·1034	223
Thorite	,,	16·6	0·0754	220
Monazite	Brazil	0·76	0·0034	223

Boltwood points out that since the uranium-radium ratio is constant within the limit of experimental error, the inevitable and only possible conclusion is that uranium is the parent of radium. He adds also that since the uranium-radium ratio in thorite, which contains about 50 per cent of thorium, is the same as in minerals, such as uranoplane and carnotite, containing a mere trace of thorium, thorium cannot possibly be regarded as the parent of radium.

He tested thirteen such minerals for lead, and found an appreciable quantity in all, except in a specimen of uranoplane, which contains a mere trace, and which is the youngest geologically. Lead minerals do not exist side by side with most of the minerals tested, so that this possible source of lead is excluded.

In a later paper Boltwood examined previously published analyses of uranium minerals; the ratio of lead to uranium in forty-three minerals varies from 0·04 to 0·25. Minerals from the same locality show very good agreement. He quotes Barrell's opinion that the variations of the ratio for minerals from different localities "are not contradictory to the order of the ages attributed by geologists to the formations in which the different minerals occur." Assuming that the helium in minerals is formed by disintegration (this statement will be discussed immediately), and according to the equation—

$$\text{Uranium } (238{\cdot}5) = \text{lead } (206{\cdot}9) + \text{helium } (31{\cdot}6)$$

(this assumes that helium is identical with the α particle and that eight α particles are liberated in the uranium disintegration)—he finds that the actual amount of helium in minerals never exceeds the theoretical quantity, and

varies from 6—100 per cent. of that quantity. The denser minerals usually retain the larger proportion.

The results of a direct spectroscopic attack on the final disintegration product of the uranium series have just been published by J. A. Gray. He considered that in most of the minerals examined by Boltwood there was possibility of accidental lead contamination. The hydrated calcium and copper phosphates (autunite and torbernite) are found in nature, and have the appearance of artificially purified substances. They are undoubtedly derived from the comparatively recent recrystallisation from water of salts derived from the pitchblende lodes. Lead has not been considered as present in them. Gray used the spectroscopic method of detection. He held that all the lines in the spectrum which could not be accounted for obviously might be considered as those of disintegration elements of the series. He used calcium chloride as a flux for the mineral, burning it between carbon arcs. As comparison spectra he employed uranium oxide and the iron arc, obtaining the three photos on one plate, so that direct comparison was possible. He examined two autunities and one torbernite. In the former cases only the lines of uranium, calcium, barium, strontium, lead and iron were present. In the third case there were also copper lines; calcium invariably contains traces of barium and strontium, and traces of iron occur in practically every mineral. Only lead is unaccounted for, and this he regards as the disintegration product.

Strutt has analysed twenty minerals for radium and uranium, and his figures, although they show greater

variation than those of Boltwood, yet point conclusively to the same result. Mlle. Gleditsch is at present engaged in re-examining the constancy of the ratio. Her preliminary results, published in 1908, do not altogether agree with the above. She has examined a Joachimsthal pitchblende, an autunite, and a Ceylon thorianite. The radium was determined directly by precipitating it with barium sulphate, and thereafter by radioactivity measurements. The Ra : Ur ratio was too small in autunite, too great in thorianite, and no reason is yet put forward. Her further results must be awaited with interest.

M'Coy and Ross found that the total radioactivity of minerals free from thorium, but containing actinium, bears a constant relation to the amount of uranium present. This led them to the conclusion that actinium is also a product of uranium. As it has been shown (*see* Chapter V., p. 41) that actinium is not in the uranium-radium series, this would point to the existence of an entirely different uranium-actinium series of disintegrations.

Szilard has shown that uranium minerals which do not contain thorium contain both ionium and actinium; he regards this as supporting M'Coy and Ross's intention that uranium is the common parent. The possible common parent might be uranium X.

Soddy has calculated, from Boltwood's researches on the proportionate α radiation contributed by the separate constituents in equilibrium in uranium minerals, that of eight atoms of uranium seven go to form radium, one to form actinium.

Since he found that all thorium minerals contain readily

detectable quantities of uranium, while some uranium minerals are practically free from thorium, Strutt concluded that uranium is derived from thorium. Boltwood pointed out that in the former case the minerals were much older than in the latter; he thinks the evidence can be interpreted on the assumption that thorium is a disintegration product of uranium having a longer life.

There is thus at least a possibility, so far as present evidence goes, that uranium is the parent of all the radioactive elements.

Since Ramsay discovered helium in the mineral cleveite, in which it exists in comparatively large amount, and since Lord Rayleigh proved its existence in the Bath waters, many workers have turned their attention to the existence of the rare gases in minerals and springs. Since Ramsay and Soddy showed that helium is a disintegration product of radium, investigators have tried to discover some relation between the amounts of radioactivity and of rare gases present. Strutt and Moureu have paid special attention to this problem.

Strutt has made an exhaustive study of the composition of radioactive minerals, especially to ascertain the relative proportions of uranium-radium, thorium, and helium present. In his initial experiments he heated the mineral with strong sulphuric acid to obtain its gaseous constituents. These were analysed by methods similar to those described on p. 16, *et seq.*

It has been mentioned already that Boltwood has considered the presence of helium in minerals as derived from uranium, neglecting the possible production from thorium.

Strutt strongly disputes this view, and his results bear out this opinion. The following figures are taken from a paper which he published in 1905:

Mineral.	Locality.	Helium c.c. per kilogram.	ThO_2 per cent.	Radium as radium bromide, millionths per cent.
Thorianite	Ceylon	8·9	77·0	30·4
Monazite	Norway	2·41	1·21	0·275
Samarskite	N. Carolina	1·50	1·46	22·5
Monazite	Fahlun	1·40	0·80	0·323
Aeschynite	Hitteroe	1·09	1·26	24·0
,,	Urals	0·98	8·18	9·90
Orangite	Brevig	0·11	48·5	2·82
Pitchblende	Joachimsthal	0·107	—	153·0
,,	Cornwall	0·10	—	48·5
Cupro-uranite	,,	0·10	—	120·0
Microlite	Virginia	0·05	—	3·70

Strutt points out that in no case does any mineral contain more than a trace of helium unless thorium is also present. When much helium is present, thorium is present in quantity; but the converse is not true, as is shown by the case of orangite.

Later he quotes the case of the mineral fluorite, from Ivigut, Greenland, which yields 27 c.c. of helium per kilogram, contains scarcely any radium, but is rich in thorium. He concludes that the production of helium from thorium must be considered to be established.

Note must be made in passing of the peculiar fact that pitchblende and cupro-uranite, two of the most strongly radioactive minerals known, yield only minute traces of helium.

These anomalies are perhaps explained by his recent observation that the helium in most helium-containing minerals is continually leaking out, and that over

long periods the loss in many cases must be considerable.

In a paper published in the present year Strutt tabulates his results for a very large number of minerals, which were examined in order to observe whether (*a*) the degree of radioactivity is sufficient to account for the quantity of helium present, (*b*) argon and neon are present in definite amount.

He finds that helium is present in almost all the minerals of the earth's crust, and is roughly proportional to the traces of uranium and radium they contain. When there is much more helium than would be expected from the amounts of uranium and radium present, it can always be connected with the presence of thorium, with one exception. There is no evidence that helium is produced from ordinary elements.

The mineral beryl contains abundance of helium, but is only very slightly radioactive. The helium cannot be connected with any known constituent of beryl.

With regard to argon, its presence in small quantities is probably due to traces of atmospheric air leaking into the apparatus. Nevertheless it is certainly present in igneous rocks, and probably in siliceous minerals generally. No definite conclusion is reached with regard to the presence of neon. It has been observed in several cases; but Strutt states that an admixture of one cubic centimetre of air makes the neon spectrum visible, and that it may even be seen with one-tenth of a cubic centimetre.

Strutt has examined a large number of saline minerals.

He finds that sylvine and carnallite, both potassium minerals, contain considerable quantities of helium, although but very slightly radioactive. He suggests that the helium is derived from the potassium. So far, however, potassium has been found to emit only β rays. It is possible that α rays are emitted, of such relatively small velocity and penetrability as to be barely detectable, or even quite undetectable.

Hogley has examined malacone, a zirconium mineral, for argon. He obtained almost pure helium, accompanied by 1 per cent. of argon. The presence of argon in malacone had previously been affirmed by Kitchen and Winterson, and by von Antropoff. Again Travers, Senter and Jacquerod state that an appreciable quantity of krypton was obtained from the mineral cleveite. Hogley examined the similar mineral fergusonite, with negative results.

So far as the experimental results to date tell us, the occurrence of other of the inactive series other than helium in minerals must be regarded as still problematical.

The general results derived from the examination of the gases from springs leads to the conclusion that they are all more or less radioactive, and all contain traces of the rare gases. This is only to be expected in the light of the general presence of radioactive matter in minerals and rocks generally, through some of which the spring waters must percolate.

Coming to particular examples, Rayleigh, as has already been stated, detected helium in the gases from

the Bath waters, and the amount is such that Dewar was able to employ them as a source of helium.

Moureu has examined the gases from over forty different hot springs throughout France. In all cases rare gases were present in quantities varying from 0·005—6·35 per cent. Of these argon was detected spectroscopically in forty-three cases, helium in thirty-nine. Usually the quantities were of the same order of magnitude. No separation of the two was attempted. Moureu states that his figures agree with the radioactivity of the springs as determined by Curie and Laborde. The larger part of the gases always consisted of nitrogen and carbon dioxide; oxygen was only present in small amount. The rare gases were proportional to the nitrogen, inversely to the carbon dioxide. It is hence at least possible that the argon detected by Moureu had, like the nitrogen, originally an atmospheric origin.

In later work Moureu has shown that traces of neon are usually found. Since his methods were similar to those used by Strutt, the remarks of the latter must be borne in mind *re* the possibility of air-leakage accounting for small traces of neon. Incidentally, Moureu and Biquard estimate that a spring at Bourbon-Lancy produces over ten thousand litres of helium annually, although this only amounts to 1·84 per cent. of the total gas evolved. So that there is some ground for believing that at any rate all the helium in the atmosphere is ultimately derived from radioactive changes.

Cady and M'Farland have detected helium in forty samples of natural gas from widely separated parts of America. They observed neon in one instance.

The number of spring waters all over the globe in which the presence of radioactive matter and of rare gases is being recorded is continually on the increase.

In view of the experiments of Ramsay and Cameron on the production of lithium and other alkali metals from copper, M'Coy and Mlle. Gleditsch have determined the amounts of copper and lithium in several radioactive minerals.

M'Coy found that four uranium-radium minerals contained both copper and lithium in easily recognisable amounts, while a fifth, a sample of gummite, contained lithium, but no copper. He considered that these results agreed with the possibility of a transformation from copper to lithium.

Mlle. Gleditsch has examined a number of radioactive minerals from different sources. They all contain lithium but in quantity which can only be determined spectroscopically. She finds that there exists no simple relation between the copper and lithium present in such minerals, whilst the mineral which contains the largest amount of lithium, a sample of carnotite, is one of the least radioactive. She concludes that whilst the results do not contradict Ramsay's theory, neither do they support it.

CHAPTER XII

RECENT RESULTS AND SPECULATIONS

The theory of disintegration advanced by Rutherford and Soddy in 1903 has stood the test of further discovery remarkably well. They postulated, it will be remembered, that radioactive changes were really successive degradations of the elements, and that when these were accompanied by the emission of α particles, the element produced differed in atomic weight by four from its parent element. The fact that it is now established that the α particle is in reality an atom of helium of atomic weight 3·96 lends great strength to their argument. This is further supported by the discovery of ionium and the proof that radium is the descendant of uranium. It is true that the difference in their atomic weights is $(238{\cdot}5 - 226{\cdot}5) = 12$, equivalent to three α particles, whereas only uranium and ionium have been proved to have an α radiation. It was at first thought that uranium X emitted α rays, but the balance of experiment is against this. It is probable that a further intermediate α-producing element will be discovered, and indeed Danne has already announced the existence of what he calls *radio-uranium*, intermediate between uranium and uranium X.*

* Soddy's most recent work points on the other hand to the existence of this unknown element between uranium X and radium. The uranium-radium descent is engaging the attention of several workers, and will probably be defined accurately shortly.

The strong grounds for the belief that the final products of radium series is lead, and the close agreement in the calculation

Atomic weight of radium	−	5 α particles	=	atomic weight of lead
226·5	−	(5 × 4)	=	(206·5) 207

also support the theory. But this assumption necessitates the condition that the atomic weight of the emanation is (226·5 − 4) = 222·5, whereas we have seen that there is good experimental ground for the belief that it is 176. The only experiment evidence put forward for the higher weight is that of Perkins, though this is strong. The close agreement between the calculated and found data for the volume of the emanation does not come into the question, as the only assumption made was that one atom of radium emitted one atom of emanation.

Ramsay and Gray have suggested the possibility of a change as

Ra	=	He	+	x	+	Em	or	Ra	=	2 He	+	x	+	Em
226		4		46		176		226		8		42		176

where x is a non-radioactive element.

It is evident that should the lower atomic weight be correct the original theory will require considerable modification, and the harmonious sequence of changes cannot hold. Further work in this direction is therefore awaited with great interest.

Three other results have appeared recently somewhat unsettling of previous convictions. The first is Mlle. Gleditsch's recent work on the non-constancy of the uranium-radium ratio (p. 131), and this has also a direct bearing on the theory.

The second is the independent observance by Debierne and by Rutherford (p. 32) that the half-life period of the emanation appears to differ with different portions of emanation. For example, they each noticed that when the emanation was condensed at the temperature of liquid air, the part which could be pumped off first had a longer life period than that which remained, and this pointed to the emanation being divisible into portions with different boiling points.

Finally, the curious cessation of decomposition of water in a radium salt solution, observed by Ramsay, should not be forgotten. The normal yield fell for a month from 25 cubic centimetres of mixed gases a week to practically nil. So far no explanation has been put forward.

Accepting in the meantime the general truth of the theory of disintegration, it is of some interest to speculate as to how these numerous new elements fit into the periodic table. Many arrangements have been proposed, in nearly all of which the attempt has been made to fit each element into a *separate* place in the table.

There seem to be numerous grounds for regarding any such attempt as a mistake. The number of spaces vacant for elements of weight less than uranium are too few for the number in the uranium and thorium groups alone. The atomic weights of uranium, thorium and radium may be regarded as definitely fixed within one unit. There is very strong evidence for the belief that the atomic weights of the emanations of thorium and radium differ

by only one or two units. Their co-efficients of diffusion are practically the same. Under the same pressures they condense at nearly the same temperatures. Again, intermediate between thorium and its emanation comes the element radiothorium, which resembles radium in every respect. Unless the theory of Rutherford and Soddy is wrong *ab initio*, we must suppose that radiothorium and radium occupy the same space in the periodic table. On similar grounds it seems probable that in most cases at least two of these radioactive elements occupy the same space. With regard to the actinium series nothing definite can be stated until the atomic weight of actinium has been determined. But the actinium series resembles those of the two others strongly and seems to fit into the same groove.

Cameron has recently suggested a form of the periodic table which fits all the known facts and makes only three assumptions.

1. More than one element can occupy the same space.

2. The emission of an α particle necessitates transference to a space of lower atomic weight.

3. The emission of a β particle, or the occurrence of a rayless change, may, or may not, be accompanied by such a transference.

His arrangement is shown on following page.

								H 1
He 4	Li 7	Be 9	B 11	C 12	N 14	O 61	Fl 19	
Ne 20	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35·5	
Ar 40	*K* 39	Ca 40	Se 44	Ti 48	V 51	Cr 52	Mn 55	Fe Co Ni 56 59 59
	Cu 63·5	Zn 65	Ga 70	Ge 72	As 75	Se 79	Br 80	
Kr 83	*Rb* 85	Sr 88	Y 89	Zr 90	Cb 93·5	Mo 96	Np? 100?	Ru Rh Pd 102 103 107
	Ag 108	Cd 112	In 115	Sn 119	Sb 120	Te 127·5	I 127	
Xe 131	Cs 133	Ba 137	La 139	Ce etc. 140-178	Ta 181	W 184		Os Ir Pt 191 193 195
	Au 197	Hg 200	Tl 204	Pb 207	Bi 208 ← **RaF** ← E_2 ← E_1 ← *D*	? ← *Act C* ← **ThC** ← **RaC** ← *RaB*	← **ActB** ← *ActA* ← **ThB** ← *ThA* ← **RaA**	
← **Act Em** ← **Th Em** ← **Ra Em**	← **Act X** ← **Th X** ← *Ra X*?	← **Radioact** ← **Radioth** ← **Ra** 226·5	← *Act* ← *Mesoth 2* ← *Mesoth 1* ← **Ionium**	← **Th** 232·5 ← *Ur X*	← **Radio Ur?**	← **U** 238·5		

Such a theory is not unlikely when we consider the certain complex internal structure of the elements of high atomic weight. We can compare them with organic compounds of the same molecular weight, in which often a slight change in constitution involves a considerable change in properties, while two compounds with but a slight difference in their molecular weights often have marked resemblance.

A rayless change, or one involving the emission of β particles, can be compared to the frequent formation of one desmotropic substance from another under the influence of heat.

It may be pointed out that there are three α-emitting elements between radium emanation and lead, and only three vacant spaces in the table, and two α-emitting particles between thorium emanation and bismuth, with two corresponding spaces. Is the final product of the actinium series the element of the titanium group so long suspected to exist in titanium itself, and still looked for in spite of Brereton-Baker's recent work?

Again it may be emphasised that the anomalous existence of the group of rare earth metals near the centre of the table, giving a difference of 41 between cerium and tantalum, explains the rise in the difference between two consecutive members of a vertical column from 46 to nearly twice that figure, so that no element of the argon series is to be expected between xenon and one at about 220. There is no space for an emanation at 176. Except in the two spaces above manganese (one of which may be filled by nipponium), and possibly in the rare earth series, *there are no vacant spaces in the periodic table*

between hydrogen and uranium. In this connection it is interesting to recall the suggestion of R. W. Wood that the green line in the spectrum of the sun's corona is the fluorescent line of some common element, and that the element coronium in whose spectrum this line was supposed to be, and which was presumed to have a weight less than hydrogen, does not exist.

It is possible that other β-emitting or rayless elements may be discovered. How far these are really *elements* depends of course on the *specific* physical and chemical properties they are found to possess. Hahn has recently put forward the assumption that no element can emit both α and β rays. He has proved apparently that radium emits β rays, and has postulated a hypothetical radium X (the existence of such an element is at least likely; see the periodic table), and further has tried to resolve radium C, a typical element emitting the two kinds of rays, into two substances.

If, as there is now strong reason to believe, the number of α-emitting elements is complete, it is surely time that the useful but clumsy nomenclature for these elements should be replaced by permanent names.

It has been pointed out that it is at least possible that uranium is not only the progenitor of the radium series, but also of those of thorium and ionium(p. 132). Soddy has recently endeavoured to give a theory of how such a process can come about. He considers that since the disintegration of a particular atom simply depends on the law of probability, and for any atom selected at random is quite an uncertain quantity, so moreover is

the kind of disintegration, and whether the result will belong to one series or the other. The exponential law will still hold, though the actual time rate will be different to that which would exist were the disintegration of one kind only.

This theory still does not admit of such changes as those suggested by Ramsay and Gray, where the breakdown of one atom is supposed to result in the production of three or more (p. 139).

Strömholm and Svedburg are studying the chemical nature of the radioactive elements by means of the isomorphous relationships of their salts. They point out that small quantities of impurities are invariably carried out of solution by precipitates, and claim that in consequence no stress can be laid on the chemical properties of such elements found in this way. They have observed that thorium X is isomorphous with barium and lead, while thorium, mesothorium 1 and 2, and radiothorium, are all isomorphous with the rare earths.

Now that it has been proved that one element can be transformed into another, it is inevitable that attempts should be made to explain these facts, and at the same time to suggest a reasonable theory of element-synthesis.

Prout's hypothesis has been revived in new guise. At no time can it be said to have altogether lost support. As originally put forward, it was easily proved untenable, with the advent of exact atomic weight determinations. Nevertheless, the periodic system, and latterly

spectroscopic evidence, pointed ever more strongly to some underlying relationship between all the elements. And the development of radioactivity once more concentrated attention on these ideas.

Lockyer, considering the spectra of nebulæ, of which the degree of complexity increases as the nebula gets less simple, considers that this points to a gradual building up of elements from the simplest forms.

Perhaps the most ingenious of recent theories of element-synthesis is that put forward by A. C. and A. E. Jessup, which starts with the same idea. From spectroscopic evidence they conclude that matter in the nebula stage consists of four elements, termed *protons;* of these, two only, hydrogen and helium, are known. These protons are formed from primary corpuscles—the original form of matter—by aggregation into stable integral systems. Other atoms are formed by a process of condensation of corpuscles round the proton-groups, the various atoms representing groups of maximum stability in a gradual and continual process. The authors state that the formation of successive elements is attended by the escape of a large quantity of energy; the systems are steadily progressing from higher to lower energy content. "The whole process of evolution is entirely governed by the possibility of energy leaving the system." They suggest instability as the reason of disintegration, and this is undoubtedly true. The fact, however, that radioactive disintegration releases an enormous amount of energy (compare p. 50) seems fatal to their argument just quoted. For it is difficult to see how a building-up process, consisting of a coalescence of two elements to

form a new one with liberation of energy, can be harmonised with a breaking-down process, consisting of the production of two elements from one, also with liberation of energy.*

Egerton has recently succeeded in giving a scientific basis to Prout's hypothesis. He finds that the atomic weights of all the lighter elements can be expressed as simple multiples of that of hydrogen, plus or minus a certain definite number of electrons (the weight of an electron being one-thousandth that of a hydrogen atom). This number of electrons bears a simple relation to the whole number in question, and it is this simple relationship, and the regular numerical gradation which it follows, which differentiates this paper from the great mass of work having the same end in view.

It is highly probable that ultimately we shall be in possession of some theory which will account for both the evolution and devolution of the elements, and we may be able even to find cases of evolution going on, or to cause them to take place. So far, however, we do not possess even a theory which seems to satisfy all the facts.

* This statement should, perhaps, be modified. It is possible, though unlikely, that two elements *a* and *b*, can give rise to a third *c*, plus energy, and that this can disintegrate into *d* and helium, and free energy. In this case, *d* must differ from *a*, and *b*.

CHAPTER XIII

RADIOGEOLOGY

In the last chapter I have mentioned theories concerned with the building up and breaking down of atoms. The branch of our subject connected with geology is even more interesting and fascinating; it may even be connected with the building up and breaking down of worlds. I am unable to give more than a brief abstract of the results obtained, for which I am largely indebted to the recently-published book, *Radioactivity and Geology*, by Joly, who, with Strutt and Eve, is one of the pioneers of this line of research. For further details readers are referred to this, and to the original papers, to which reference is there given.

It has been indicated in Chapter XI that the elements of the uranium-radium and thorium series exist in numerous minerals in relatively large amount. But their existence, of course in far smaller amount, in all ordinary material, and in sea water, is quite large enough to be measurable, while the radium and thorium emanations exist to a measurable degree in ordinary air, whether over land or ocean, since the *natural leak* of an electroscope is due to the continuous production of ions by traces of these gases. The amounts of radium and uranium in ordinary materials are measured, as has been indicated in Chapter XI, by the amount of emanation which can be driven off from it in solution. The following figures,

obtained in this way, give an indication of the widespread diffusion of the radioactive elements.

Strutt made a large series of experiments with igneous and sedimentary rocks from widely different sources, and his figures are:

Mean radium content per gram igneous rock, $1{\cdot}7 \times 10^{-12}$ gram.

Mean radium content per gram sedimentary rock, $1{\cdot}1 \times 10^{-12}$ gram.

Eve obtained very similar results with specimens of different rocks in the neighbourhood of Montreal.

Joly examined 92 specimens of igneous rocks from all over the earth's surface; many of the specimens were obtained at considerable depths. The mean radium content per gram material was $6{\cdot}2 \times 10^{-12}$. From 63 rocks of sedimentary origin he obtained the figure $4{\cdot}7 \times 10^{-12}$. Rejecting doubtful cases, he regards the minimum figures at certainly not less than 5 and 4 ($\times 10^{-12}$) respectively.

His mean for 24 determinations of sea water from various portions of the globe was $0{\cdot}017 \times 10^{-12}$ gram radium per cubic centimetre. He calculates that in the combined ocean volumes there exists not less than 20,000 tons of radium. As deep-sea deposits are found to be richer in radioactive material than dry land, while river water is less radioactive than sea water, Joly considers that the radium in the ocean must be derived from beneath it, and estimates that the ocean bed must contain well over a million tons of it.

These results give an idea of the absolute scattering of the radioactive material over the earth's surface. It is

interesting to note in passing that although any given land surface contains far more radium than an equal extent of ocean surface, yet Eve has found that in the calmest weather, when a minimum amount of diffusion is set up by air currents, the ionisation of the atmosphere over the central portions of the Atlantic (and the corresponding amounts of emanations there) is almost the same as that over the land. The explanation is due to the greater ease with which emanation escapes from water than from solid. The radioactivity of the atmosphere can be connected with the occurrence of rain, snow, etc., since the ions act as condensation nuclei, and provide the mechanism when the amount of water vapour becomes sufficiently great.

One of the most striking effects of all radioactive changes is the liberation of heat which accompanies them, (compare p. 50 *et seq.*). Although the radioactive elements are diffused so widely that the heat change taking place at any particular place is negligible, yet when we take very large masses of material into account it becomes a factor of importance. When we recollect that it is liberated in large part in rock masses, or under similar conditions where the heat conduction is small, we can perceive that over long periods the slow rise in temperature may amount to a very considerable total effect.

The average temperature gradient at the earth's surface is about 32 metres per degree centigrade; from this it is estimated that the total annual escape of heat from the earth is of the order $2{\cdot}0 \times 10^{20}$ calories. This corresponds to 125×10^{-8} calories per square centimetre per

second. Now one gram of radium gives $5{\cdot}6 \times 10^{-2}$ calories per second. Hence, neglecting altogether the thorium series of elements, and considering the heating effect of the uranium-radium series alone, in order to equalise the present loss of heat by the earth it is only necessary that below each square centimetre of the earth's surface there be $2{\cdot}2 \times 10^{-5}$ gram of radium, or since uranium and radium in equilibrium are as 1 to $3{\cdot}4 \times 10^{-7}$, that there be 70 to 90 grams of uranium as a *maximum*.

The observed average radium content in igneous rocks is as a *minimum* 5×10^{-12} gram per gram; consequently there must be a maximum thickness of crust of such rocks of only 27·5 to 37·5 kilometres in order to neutralise the earth's loss of heat.

It is evident that if the observed percentage of radium-uranium held for rocks still deeper, a marked heating effect would become apparent. Since this is not the case, the only other hypothesis is that the uranium has become concentrated at the earth's surface, while further inwards the proportion is much smaller. The question arises, does *any* uranium exist in the earth's interior. If it does to an appreciable extent, then the earth's interior must be gaining in temperature, since the amount at the surface is sufficient to neutralise the quantity lost outwards by radiation. But no such gain in temperature has been observed.

Kelvin has shown that an immense length of time must pass before the earth's interior can cool appreciably by heat radiation to the surface. He calculated that if the specific heat and thermal conditions are the same as with surface rocks, even after a thousand million years

there would have occurred no sensible loss from an interior core equal to one half of the earth's volume. Similarly we can argue that a tremendous length of time would occur before a heating effect became perceptible. Under all ordinary conditions we should expect that any element existing at the earth's surface also existed in some greater or smaller quantity throughout; there appears to exist no reason that uranium should be an exception.

Therefore, Joly concludes, the earth's interior temperature is rising. If the supply of heat is large enough the effects must *ultimately* be felt at the surface; but if very slow, then the decay of the uranium itself may intervene and a surface effect never become apparent.

"Wonderful possibilities are brought before us. Peaceful cooling may await the earth, or catastrophic heating may lead in a new era of life. Our geological age may have been preceded by other ages, every trace of which has perished in the regeneration which has heralded our own.

"Whatever be the future or the past of our world, we have the untrammelled regions of space in which such varied destinies must surely find their accomplishment. The planets may now be in varying phases of such great events. And when a star appears in the heavens, where before we knew of none, may not this be a manifestation of the power of the infinitely little over the infinitely great—the unending flow of energy from the unstable atoms wrecking the stability of a world."

A physical explanation of the surface concentration of

uranium has been put forward. It is supposed that the earth was originally formed from the sun, where local variations of material also exist, so that the uranium was always to some extent concentrated, even in the molten earth. The masses of molten material containing the uranium were heated to even higher temperature by the radioactive changes, and convection currents resulted, which forced the masses to the surface where they solidified.

Even there it is held probable that the uranium exercises a heating effect which under certain conditions of surface strain supplies the necessary stimulus for mountain elevation and volcanic and earthquake phenomena.

On the other hand, it has been pointed out that the sun at present must be cooling, as even though it were very largely composed of uranium insufficient heat could be supplied from this to neutralise the enormous loss by radiation.

There is reason to believe that thorium is as important a factor as uranium in these calculations, and in consequence the results obtained become even more striking.

It is necessary, in conclusion, to discuss how the discovery of the properties of radioactive material has affected calculations of the age of our planet. From the assumptions currently accepted up to within the last two decades, that the earth consisted originally of an incandescent fluid mass, and that by loss of heat it had solidified and was still growing cooler, Kelvin calculated the time which had elapsed since the initial solidification. His results were based on the loss of heat necessary to give

the present heat gradient at the earth's surface; his final figure was in the neighbourhood of a forty million years' period since solidification.

Various estimates have been made on geological data. For example, Sir A. Geikie compared the thickness of sedimentary rocks with the rate at which sediment is borne from the land and deposited on the ocean floor. His figure is approximately a hundred million years, of a different order to Kelvin's, and since it presupposes the earth in a more advanced condition the time since solidification must have been considerably greater.

The utilisation of heat from radioactive sources to counterbalance the loss due to normal cooling would necessarily increase the estimate of age based on Kelvin's calculations and reconcile it with the figures derived from geological data.

Most of the uranium and thorium minerals contain helium, and as we can accept as a fact that its presence here is due to the radioactive changes in the minerals, a method is suggested for finding their ages. This was first utilised by Strutt. Theoretically a mineral containing one gram of radium in radioactive equilibrium with uranium and with its products emits 316 cubic millimetres of helium per year. (Cp. pp. 103 and 106. Dewar's experimental figure is 270 cubic millimetres.) The mineral fergusonite contains 1·81 cubic centimetres of helium, and $0{\cdot}75 \times 10^{-8}$ gram radium per gram mineral. Its life, calculated from this data, is 241 million years.

Strutt's figure for an early sample of hæmatite is 141 million years.

These figures are much greater than those calculated from geological data, and moreover, they are all *minima*, since Strutt has shown that quite perceptible leakage of helium takes place from most of the minerals which he has investigated.

Strutt has varied the method of attack, using actually laboratory experiments. He dissolved a specimen of thorianite in acids and by prolonged boiling drove off all the helium. Then he allowed the whole to remain for seven weeks, again drove off all the helium and measured it. It was a just measurable quantity. Taking the total amount of gas measured as helium (2×10^{-6} c.c. in seven weeks from 400 grams of thorianite), the *maximum* rate of production is $3{\cdot}7 \times 10^{-8}$ c.c. per year per gram mineral. The thorianite originally contained 98 c.c. helium per gram mineral, so that the minimum age of thorianite is 240 million years. Since Strutt suspected that his measured helium was two-thirds impurities, it is possible that the real age may even be over 700 millions.

By similar methods the various geological periods can be fixed in time more or less accurately.

It is interesting to notice, as Soddy has pointed out, that although thorianite is an extremely old mineral geologically, yet if the thorium is originally formed from uranium (compare p. 132) the mineral must really be of recent formation. Another explanation of this can be suggested. The uranium thorium change might take place equally well while the earth was in a state of incandescence, without separation of the two elements, and hence no arguments on the age of the earth can be

based on the assumption of a uranium-thorium degradation.

I conclude this chapter with a map of the world, recently published by Szilard in *Le Radium* (fig. 15), which shows the localities of the uranium and thorium minerals hitherto investigated. No conclusions can be drawn from the distribution here indicated, since the list of minerals examined is not exhaustive, and others may be found in hitherto unsuspected localities.

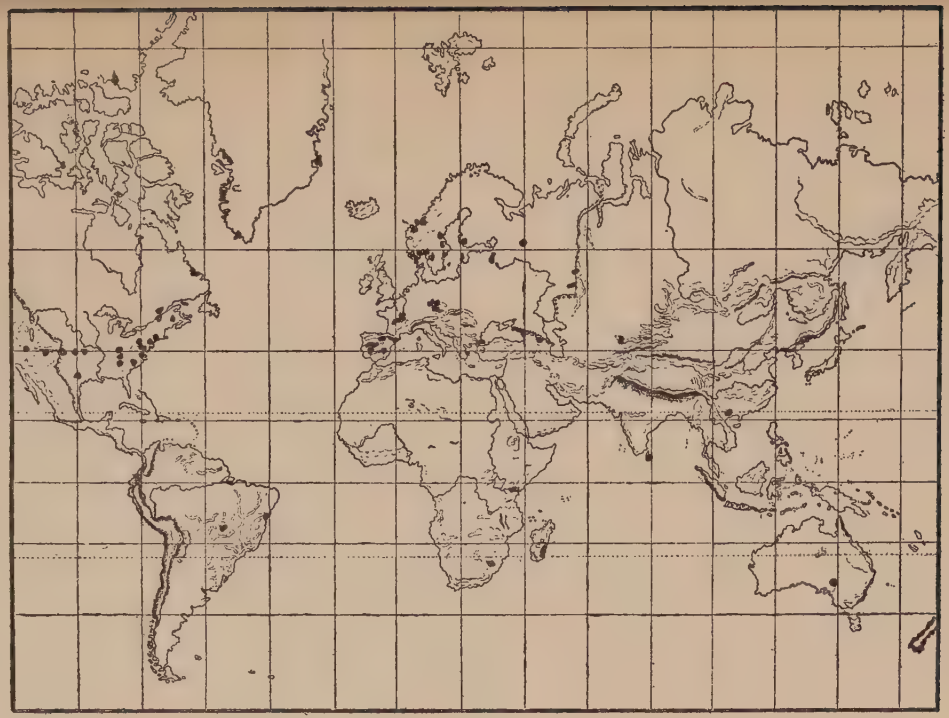

FIG. 15.

Reproduced from *Le Radium* for August 1909. By permission of Messrs Masson et Cié.

CHAPTER XIV

THE MEDICAL APPLICATION OF THE RADIATIONS

BECQUEREL, who made the initial discovery which led to radioactivity becoming a science, made also that which led to its use in therapeutics. The latter was accidental. In 1901 he carried a small tube containing radium in his waistcoat pocket for a few hours only. After fifteen days the skin became inflamed. A " burn " developed, and the effect was traced to the action of the radium.

Since then very much work has been done on the subject. The therapeutic action was found similar to that of the X-rays, but even more extended. Should the action only be the same the advantage possessed by radium preparations in transportability and convenience in applicability is at once apparent.

The first institute to systematically study the therapeutic effects was the "Laboratoire biologique du radium," established in Paris in July 1906. The radium was furnished by Armet de Lisle, and the direction of the pathological experiments was given to Dr Wickham. The results of three years' systematic work has just appeared in the volume, *Radiumthérapie*, by Wickham and Degrais, to which I am indebted for what follows.

Applications have been carried out in numerous ways. The following are the chief methods employed:

1. The emanation from radium is inhaled. The radium salt is dissolved in water in an apparatus closed by two taps, and from time to time air is drawn through and carries away the emanation with it. It is this mixture which is inhaled.

(*b*) The same mixture is passed through a tube at liquid air temperature, where the emanation is caused to condense on suitable substances. These can be of two kinds: (1) water, vaseline, lanoline, oil, glycerine, etc., having no specific effect themselves, and which can be injected or applied externally; (2) quinine, arsenic, mercury, bismuth, subnitrate, etc., taken internally, and giving a joint effect.

2. Very dilute solutions of radium salts are made up and injected. These then become comparable with naturally-occurring radioactive waters.

3. Insoluble radium salts are suspended in liquids and injected. It has been shown that it is thus possible to localise the radium in certain tissues, but the method is too costly for ordinary use.

4. Methods by the direct external action of the rays. These are the methods hitherto regarded as most important. The present forms of apparatus employed are of three kinds. Glass tubes containing the radium salt are used especially for action on the internal mucous membranes, as in the mouth or nose. Copper plates with roughened surfaces are covered with a thin layer of suitable varnish containing the radium salt well mixed, so as to give a uniform radiating action. This is the form

chiefly employed. Linen cloths are covered with the varnish. They possess the greater advantage of flexibility.

In making an external application the surface of the skin is protected by lead foil, in which is cut an aperture corresponding to the diseased tissue. The instrument containing the radium deposit, protected by very thin muslin, is applied directly, so that all, even a proportion of the *a* rays emitted, produce an effect. The following cases give an idea of the kind of treatment and the result obtained.

A budding epithelioma was removed after thirty applications, each of an hour's duration, spread over twenty-two days, of radium corresponding to activity 50,000, comprising 0 % α rays, 85—90 % β rays, and 10—15 % λ rays.

An ulcerated sore was healed with the same quantity of radium by eight one-hour applications at two-day intervals.

Two keloids were absolutely removed by three applications, each of half an hour, at intervals of three days, with radium activity 48,000, comprising 0 % α, 89 % β, and 11 % λ rays.

A neurodermititis disappeared after four applications of twenty minutes each, spaced over forty days, with an apparatus of 20,000 radioactivity, comprising 15 % α, 73 % β, and 12 % λ rays.

In considering these figures it must be remembered that with the instruments employed the amount of radium present is not the factor of importance but the

amount of radiations emitted and utilisable. These are measured electrically. As in their chemical effects, the different radiations appear to have no differing qualitative effects*; only the quantitative effect produced varies with the nature of the ray.

The action on different tissues varies considerably, and with it the necessary duration of treatment. The nature of the action also varies in marked degree. In some cases there is no trace of inflammation, in others, all degrees of inflammation may be present. Some kinds of tissue can be influenced with ease, others only with great difficulty.

The number of diseases which can be treated beneficially is very great. Most marked effects are produced with ulcerous growths, lupus, birth-marks, and scars. The most developed cases disappear, leaving, even in extremely bad cases of lupus, scarcely a differing shade of colour to indicate that they had existed. In many cases no trace of previous diseased tissue can be seen. Superficial cancer and tubercular growths yield to the treatment. It is doubtful whether cases of deep-seated cancer have yet been definitely cured.

Some indication of the nature and different kinds of the effects is given in the table following, which is translated from that on p. 100, *Radiumthérapie*.

* The α ray effects are, however, so strong as to cease to be beneficial.

A. *Therapeutic actions.* Doses properly regulated.

- Exerted on pathological tissues more or less extended in depth, and affecting the cutaneous or mucous surface,
  - (*a*) Without an ulcerated phase and without irritation of the surface. — This form of action exists only for the diseases which depend on the selective specific action of radium. — Examples: keloids, cancers, eczemas, angiomes, etc.
  - (*b*) With ulcerated phase, exerted at the surface of the tissues.
    - (*a*) For the reactions of the first group where this action is not *necessary* it is still *useful*, as a practical device to gain time. — In this case there is a combination of specific and destructive action in diverse degrees. There is a destructive action at the surface, a specific beneath.
    - (*b*) This mode of the action is necessary for the diseases which do not seem to be dependent on the selective action of radium. That is to say, in order to heal these lesions it is necessary to have recourse to the destructive power of radium, and to count on the value of the tissues of repair. — Examples: coloured birthmarks, fibro-sclerotic bands, tuberculoses, etc.
- Exerted on pathological tissues more or less extended in depth, but not affecting the cutaneous or mucous surface.
  - (*a*) Without an inflammatory stage visible clinically. — When the affection arises from the specific action. — Examples: cancers, vascular tumours.
  - (*b*) With an inflammatory stage visible clinically. — When the disease does not arise from the specific action. In this case one is compelled to alter the surface tissue in order to destroy the pathological subjacent tissues.

B. *Nontherapeutic actions.* Errors of dose, or individual susceptibilities, idiosyncrasies.

- The action has been:
  1. Insufficient or too great.
  2. Accidental.
  3. Useless or hurtful.
- The possible result may be:
  1. A "burn."
  2. An irritation which can give stimulus to morbid evolution.
  3. Similar complications.

The recent founding, due to the generosity of Sir Ernest Cassel, of a Radium Institute in London, which will shortly be housed in a building of its own, and the similar developments in Vienna and elsewhere on the Continent, promise a rapid development of this branch of our subject.

We may expect especially, perhaps, a development of the employment of solutions of the emanation in water or other solvents, internally or by subcutaneous injections; this is by far the most efficacious means of utilising the radiations. It is interesting to recall that the beneficency of radioactive waters is quite possibly due to the activity; it is a well-known fact that we can imitate these waters chemically without producing the same medicinal effect, so that there may be a possibility of very dilute doses of the radiations acting and being utilised as a tonic.

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